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THE EFFECTS OF ADDITION AGENTS IN ZINC ELECTROWINNING FROM KIDD CREEK ELECTROLYTE

by

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ABSTRACT

The individual and combined effects of antimony, sodium silicate, Dowfroth and Saponin on zinc deposition current efficiency and polarization and on the zinc deposit morphology and preferred orientation were determined in 6-h electrolysis tests conducted at 38°C and 500 A/m^2 current density. Platinum anodes and aluminum cathodes were used with Kidd Creek electrolyte containing 55 g/L Zn and 200 g/L H_2SO_4. The trends identified in the 6-h experiments were confirmed in 24-h electrolysis tests employing Pb-Ag anodes with $SrCO_3$ additions to simulate plant operating conditions.

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Antimony depolarized zinc deposition and at concentrations >0.02 mg/L decreased the current efficiency and adversely affected the zinc deposit quality. At concentrations <0.02 mg/L, however, antimony increased the CE and improved the deposit quality. Dowfroth was found to be a strong polarizing agent which decreased the current efficiency and also had an adverse effect on deposit quality. Over a limited concentration range, certain combinations of antimony and Dowfroth maximized the current efficiency and improved deposit quality. Saponin, an alternative foaming agent, although decreasing the current efficiency, was found to be weakly polarizing and did not adversely affect deposit quality until present at relatively high concentrations. Saponin also had a beneficial interaction with low concentrations of antimony. It was observed that Saponin concentrations to 10 mg/L combined with optimum Dowfroth and antimony additions did not change significantly the current efficiency or the deposit quality. Sodium silicate alone did not affect significantly zinc deposition but it did have a negative interaction with antimony. At optimum concentrations of Dowfroth, Saponin and antimony, the addition of sodium silicate resulted in a small increase in current efficiency but did not change the deposit characteristics.

Keywords: Zinc electrowinning, addition agents, Dowfroth, Saponin, antimony, sodium silicate, current efficiency, morphology/orientation, nucleation overpotential

INTRODUCTION

The ultimate objective of this study is to determine an effective additive control strategy for the Kidd Creek zinc electrorefinery. Included in this control strategy is the development and definition of an additive operating window that will be used daily by the Kidd Creek operators. In this phase of the study, systematic laboratory tests followed by several plant evaluations were done to determine the optimum mix of the various reagents required to maximize zinc deposition current efficiency (CE) and maintain a low deposit lead content.

In industrial zinc electrowinning it is common practice to add a foaming reagent to the electrolyte to suppress the formation of acid mist over the cells in the tankhouse. The presence of the foaming agent in combination with electrolyte circulation and vigorous oxygen evolution at the anodes results in the formation of a layer of foam on the electrolyte surface that is capable of trapping most of the acid-laden gas bubbles. Dowfroth 250 (containing polypropylene glycol methyl ethers) is added primarily as a foaming agent to suppress acid mist in the Kidd Creek tankhouse. Saponin, which is used by some zinc plants for the same purpose, is also being considered by Kidd Creek either as an alternative to Dowfroth or for use in combination with a lower concentration of Dowfroth. Saponin is a steroid/triterpenoid glycoside that produces a honeycomb froth when shaken with water (1).

Current operating practice in the Kidd Creek zinc tankhouse also includes the addition of antimony and sodium silicate to control zinc deposit growth and strontium carbonate to minimize the content of lead in the zinc deposit. Antimony at concentrations >0.02 mg/L has long been recognized as one of the most detrimental impurities with respect to zinc deposition CE (2-5), and its effects have most recently been studied by Ault and Frazer (6). In spite of its detrimental effect on zinc deposition CE, a small concentration of antimony is usually added to the zinc electrolyte because it is thought to reduce zinc deposit adherence to the aluminum cathode blank. Sodium silicate is thought to have a macroscopic levelling effect on the surface of zinc deposit and thus prevent "treeing" or dendrite formation. Unlike antimony, the effect of sodium silicate on zinc electrowinning has not been studied in detail and has only been mentioned briefly in the literature (7). Strontium carbonate is thought to reduce the lead content of the zinc deposit via the formation of insoluble mixed crystals of lead and strontium sulphates that settle to the bottom of the cell with the manganese dioxide sludge (8).

Recent laboratory evaluations of alternative anodes for zinc electrowinning conducted at the Kidd Creek Metallurgical Site indicated that Dowfroth, in addition to suppressing acid mist, also had a strong influence on zinc deposition current efficiency and zinc deposit morphology. Increasing concentrations of Dowfroth resulted in a lower current efficiency and a highly

striated zinc deposit. As a result of this observation, a joint research project was developed between the Kidd Creek Division of Falconbridge Limited and CANMET to evaluate more thoroughly the effect of reagent additions to the Kidd Creek zinc electrolyte and to determine the optimum combinations required to maximize the current efficiency and improve the deposit quality.

The present study was undertaken to confirm the polarizing effect of Dowfroth and to determine its interaction with antimony and sodium silicate in Kidd Creek zinc electrolyte. The effects of Saponin, an alternative foaming agent, and its interaction with antimony, and antimony + Dowfroth + sodium silicate, on zinc electrowinning from Kidd Creek zinc electrolyte were also determined.

EXPERIMENTAL

The electrolysis cells were constructed from 5 mm polycarbonate and had the approximate outside dimensions: 8.8 x 8.8 x 10.7 cm. A tight fitting cover (5 mm polycarbonate) was modified with holes to accommodate a central aluminum cathode, two anodes spaced ~6.3 cm centre to centre, feed and spent electrolyte tubing and a thermometer. The cell held approximately 400 mL of electrolyte at 2/3 volume.

Both feed and cell electrolytes were prepared from purified neutral and cold spent solutions received from Kidd Creek. The analyses are presented in Table 1. Although these solutions contain a significant concentration of Si, Table 1, Kidd Creek

adds about 45 mg/L sodium silicate to the electrolysis feed solution presumably to prevent zinc dendrite formation. Also, both the neutral solution and cold spent electrolyte likely contain small concentrations of unidentified organic material resulting from the recycle of degraded reagents such as Dowfroth. The feed and cell electrolytes were prepared by diluting the as-received purified neutral solution with distilled water and reagent grade H_2SO_4. Some tests were also performed using the as-received cold spent solution as the cell electroltye. The feed electrolyte contained ~100 g/L Zn and ~130 g/L H_2SO_4. The cell electrolyte contained 55 g/L Zn and 200 g/L H_2SO_4. The rate of addition of feed electrolyte to the cell was adjusted so that the desired cell zinc/acid concentration remained constant for the duration of the electrolysis test. The various addition agents including Dowfroth 250, potassium antimony tartrate, Saponin and sodium silicate were supplied by Kidd Creek. These addition agents were added to both the feed and cell electrolytes at the desired concentrations as aliquots from their stock solutions which contained 600 mg/L Dowfroth 250, 30 mg/L Sb, 500 mg/L Saponin and 10 g/L sodium silicate.

The 6-h electrowinning tests were done in four cells immersed in a temperature controlled water bath to maintain the electrolyte at 38°C. The aluminum cathodes (supplied by Kidd Creek) were masked with electroplating tape to give a 2 in^2 (12.9×10^{-4} m^2) surface area. The cells were operated at

500 A/m^2 current density, and Pt anodes were used to avoid lead contamination of the zinc deposits (10).

Some tests were run for 24 hours for specific additive combinations to confirm the trends identified in the shorter experiments. For these test , Pb-Ag anodes (supplied by Kidd Creek) were used, and $SrCO_3$ was added to the electrolyte to minimize Pb contamination.

At the end of the electrolysis period, the cathodes were pulled from the cells and the zinc deposits were rinsed with water, stripped, dried and weighed. The current efficiency was calculated from the weight of zinc deposited and the number of coulombs passed. A portion of the final cell electroyte was analysed for Zn and free H_2SO_4, and the remainder was used to determine the zinc deposition polarization characteristics using cyclic voltammetry.

Sections of the deposits were examined by X-ray diffractometry (XRD) to determine their preferred orientation relative to the ASTM standard for zinc powder and by scanning electron microscopy (SEM) with a secondary electron (SE) detector to determine the deposit morphology. A portion of each 24-h zinc deposit was analysed for Pb.

Cyclic voltammetry (CV) experiments were conducted to determine the polarization characteristics of zinc deposition for both the initial and final cell electrolytes for all the tests. An aluminum disk working electrode (2.8 cm^2), a Pt foil counter electrode and a mercury/mercurous sulphate (MSE) reference

electrode were employed. The potential was cycled between -1.1 and -1.7 V vs MSE at a rate of 4 mV/s using a potentiostat driven by a voltage scan generator. The voltammograms were recorded as i vs E plots using a X-Y recorder.

A typical cyclic voltammogram (CV) for addition-free electrolyte is shown in Figure 1. A scan is initiated at point A and an appreciable current begins to flow at point B (zinc decomposition potential); the scan is reversed at point C; i.e., when the current is approximately 30 mA. At point D, the so-called crossover potential, the current is zero. After crossing point D, the current becomes anodic and zinc dissolves from the cathode; the anodic current reaches a maximum at point E and upon return to point A, zinc dissolution is complete. The region B-D is termed nucleation overpotential (NOP) and it is the difference between the crossover potential D and the point B at which zinc begins to deposit. In the present work the point B was arbitrarily chosen to be the value of the potential when a current of 2.5 mA was reached in the forward scan.

RESULTS AND DISCUSSION

The Effect of Single Addition Agents

The effects of the individual addition agents, antimony, Dowfroth, Saponin and sodium silicate on zinc deposition current efficiency and nucleation overpotential and on the morphology and orientation of 6-h deposits electrowon at 500 A/m^2 and 38°C were determined.

Antimony

The CE for the 6-h zinc deposits increased with increasing Sb concentration to a maximum value of 93.3% at 0.015 mg/L Sb; the CE then decreased with further increases in the Sb concentration, Figure 2 and Table 2. This behaviour suggests that low concentrations of Sb have a positive interaction with some species in solution (probably organic) that results in an increase in CE. The addition of Sb to the electrolyte also results in changes in the preferred deposit orientation, Table 2. As the Sb concentration increases, the orientation changes from [114][112][103][102][101] to [101][112] at the CE maximum. Further increases in the Sb concentration change the orientation back to [114][112][103][102][101] and finally to [105][103][114] for Sb ≥0.04 mg/L. These changes in the preferred deposit orientation with increasing Sb concentration are reflected in the deposit morphology shown in the series of SE micrographs, Figure 3. The addition-free deposit, Figure 3(a), consists of

irregular nodules growing on the relatively level zinc surface that is comprised of hexagonal zinc platelets aligned at intermediate angles to the Al cathode. In the presence of 0.015 mg/L Sb, the zinc deposit surface, Figure 3(b), consists of distinct, relatively compact, uniform nodules which are composed of well-defined hexagonal zinc platelets aligned to the Al cathode such that the [101] orientation predominates, Table 2. Increasing the Sb concentration to 0.03 mg/L, Figure 3(c), causes the nodules to coalesce resulting in a smooth surface consisting of hexagonal zinc platelets aligned at intermediate angles to the Al cathode. At 0.06 mg/L Sb, the deposit consists of uniform nodules composed of zinc platelets with rounded edges indicative of zinc re-solution, Figure 3(d); the platelets are aligned at low angles to the Al cathode resulting in a basal orientation, Table 2. The initial and final NOP values decreased with increasing Sb concentration indicative of depolarization of zinc deposition. These values are tabulated in Table 2 and plotted in Figure 4. The data show that the decrease in NOP with increasing Sb concentration is more rapid for Sb <0.02 mg/L and that the final NOP values are always greater than the initial values.

Dowfroth

The effect of increasing Dowfroth concentration on the CE for zinc deposition is shown in Figure 5 and the CE values together with the orientation and NOP data are presented in Table 3. The CE decreases by about 3% with the addition of

3 mg/L Dowfroth to the electrolyte; the CE then remains fairly constant to 10 mg/L Dowfroth. For Dowfroth concentrations >10 mg/L there is a gradual decrease in CE to a low value of 81.2% at 75 mg/L Dowfroth. For Dowfroth concentrations >3 mg/L, the deposit orientation changes to strongly preferred [101], Table 3, indicative of an increase in zinc deposition polarization. This is substantiated by the large increase in the initial NOP values observed for increasing Dowfroth concentration, Table 3. The final NOP values, however, remain relatively constant. The SE micrographs shown in Figure 6 indicate that Dowfroth significantly reduces the grain size of the zinc deposits thus confirming that it is a strong polarizing agent. The deposit morphology consists of uniform, closely spaced nodules, the size of which decreases with an increase in Dowfroth concentration, compare Figures 6(a) and 6(b).

Saponin

The effect of Saponin additions from 0 to 1000 mg/L on the CE for 6-h zinc deposits is summarized in Table 4 and a plot of CE vs Saponin concentration is shown in Figure 5. There is an initial decrease in CE from 91% at 0 mg/L Saponin to ~88% at 10 mg/L Saponin. Thereafter, the CE increases with increasing Saponin concentration to a maximum of ~90% at 25 mg/L Saponin. For Saponin concentrations >25 mg/L, the CE steadily decreases to a value of ~86% at 100 mg/L Saponin. At 1000 mg/L Saponin, the CE was 77.1% (Table 4) and the deposit was very brittle. The

morphologies of the 6-h zinc deposits electrowon from electrolyte containing various Saponin concentrations are shown in a series of SEM micrographs, Figure 7, and the deposit orientation results are summarized in Table 4. The addition of low concentrations of Saponin (1-10 mg/L) does not change the preferred deposit orientation which remains [114][103][102][101], Table 4. This is reflected in the deposit morphology shown in Figure 7(a) for 10 mg/L Saponin. In this case the nodules consist of hexagonal zinc platelets aligned at intermediate (30°-70°) angles to the aluminum cathode. Saponin concentrations in the range 15-30 mg/L resulted in the preferred deposit orientation becoming predominantly [112][114][103][101], Table 4. The morphology was characterized by clusters of large nodules growing on the surface of a relatively smooth layer of zinc, Figure 7(b). These large nodules consist of poorly defined hexagonal zinc platelets aligned at intermediate angles to the Al cathode. For Saponin concentrations >40 mg/L, the zinc deposit was characterized by extremes in orientation, including [100][110] (zinc platelets perpendicular to the Al cathode) and [002] (zinc platelets parallel to the Al cathode), Table 4. This type of preferred orientation was observed previously for thiourea concentrations between 10 and 200 mg/L (9), and results in the deposit morphology shown in Figure 7(c). The deposit is characterized by the growth of non-uniform, oblong particles deposited on an underlying layer of grain-refined zinc. These particles consist of layers of poorly defined zinc platelets aligned at parallel

and vertical angles to the Al cathode that give rise to the extremes in orientation, Table 4. The above results suggest that Saponin additions to zinc electrolyte have an effect on zinc deposition polarization. The NOP values for the initial and final electrolytes were obtained for Saponin additions from 0 to 1000 mg/L. These values are listed in Table 4 and are shown as plots of NOP vs Saponin concentration in Figure 8. The data indicate an increase in both the initial and final NOP value with increasing Saponin concentrations to 5 mg/L. Both NOP values then decrease to a minimum at 10 to 15 mg/L Saponin. Increasing the Saponin concentration >15 mg/L results in an increase in the NOP values which gradually level off at 40-50 mg/L Saponin. At 1000 mg/L Saponin the initial NOP is very high; i.e., 190 mV (Table 4) although the final NOP is only 145 mV. For Saponin concentrations >10 mg/L, the final NOP values are generally less than the initial NOP.

Sodium Silicate

The data obtained for the effect of sodium silicate (Na_2SiO_3) additions (0-450 mg/L) on the CE, preferred deposit orientation and nucleation overpotentials for 6-h zinc deposits electrowon at 500 A/m^2 and 38°C are summarized in Table 5. The data in Table 5 and the plot of CE vs Na_2SiO_3 concentration, Figure 5, show that the CE does not change significantly with increasing Na_2SiO_3 concentration. The deposit orientation tends to be either intermediate [114][112][103][102][101] or basal

[103][002][112][114][101] although the NOP values generally increase with increasing Na_2SiO_3 concentration, Table 5. The surface of the deposits consists of rounded nodules and isolated circular holes, Figure 9.

The Effect of Combined Addition Agents

In the previous section it was shown that concentrations of Sb ≤0.02 mg/L had a positive effect on zinc electrowinning from Kidd Creek electrolyte. In this section, the interaction of Sb with various combinations of Dowfroth, Saponin and sodium silicate is reported.

Antimony and Dowfroth

The effects of increasing Sb concentrations to 0.02 mg/L with 3-15 mg/L Dowfroth on 6-h zinc electrodeposits were investigated at 500 A/m^2 and 38°C. The CE, orientation and NOP results are presented in Table 6 and the CE data are plotted as a series of CE vs Sb curves in Figure 10. These results indicate that certain Dowfroth + Sb combinations produce a maximum CE value. As the Dowfroth concentration increases, more Sb is needed to maximize the CE. At the optimum Dowfroth + Sb combination, the maximum CE value decreases with increasing Dowfroth concentration. The optimum Dowfroth + Sb combinations that resulted in maximum CE values are presented in Table 7. For Dowfroth concentrations of 3 mg/L with various Sb concentrations and for 7 mg/L Dowfroth with either 0.015 or 0.02 mg/L Sb, the

preferred deposit orientation was [101][112], Table 6. For all other Dowfroth + Sb combinations the preferred orientation was [101]. The deposit morphology for the Dowfroth + Sb combinations which produced maximum CE values (Table 7) is shown in the series of SE micrographs, Figure 11. As indicated, the deposits consist of rounded nodules which decrease in size with increasing Dowfroth concentration. For a given Dowfroth concentration, both the initial and final NOP values decrease with increasing Sb concentration, Table 6 and Figures 12 and 13. The addition of Sb had the greatest impact on the initial NOP for electrolytes containing 3 mg/L Dowfroth, Figure 12. The initial NOP values decreased with increasing Sb and reached a minimum value at 0.01 mg/L Sb. This minimum initial NOP value also corresponded to a maximum CE value, Table 7. For the higher Dowfroth concentrations, the minimum initial NOP values occurred at higher Sb concentrations and also corresponded to maximum CE values, Table 7. The final NOP values, Figure 13, also decreased with increasing Sb concentration although the actual values were much closer to one another for a given combination of these reagents, Table 6.

Antimony and Saponin

The effect of increasing Sb concentrations to 0.03 mg/L with 1-10 mg/L Saponin on the CE for 6-h zinc deposits electrowon at 500 A/m^2 and 38°C is summarized in Table 8 and a plot of CE vs Sb concentration is presented in Figure 14. The CE increased with

increasing Sb concentration to 0.01 mg/L for all Saponin concentrations, and reached a maximum of 93.9% for 0.01 mg/L Sb and 3 mg/L Saponin, Table 8, Figure 14. For Sb concentations ≥0.02 mg/L, the CE decreased with increasing antimony concentration; the rate of decrease was greatest for the lowest Saponin concentration. For a given Sb concentration >0.02 mg/L, the CE increased with increasing Saponin. For example, at 0.03 mg/L Sb, the CE was 87.7% for 1 mg/L Saponin but was 92.5% for 10 mg/L Saponin, Table 8. In the absence of Sb, the preferred deposit orientation for each Saponin concentration was essentially [114][103][112][102][101], Table 8. The addition of 0.005 and 0.01 mg/L Sb changed the deposit orientation to [101][112]; at the higher Sb concentrations, the orientation was either [112][101][102][103][114] or [114][103][112][102][101], Table 8. The final NOP values were higher than the initial values but, as expected, both decreased with increasing Sb concentration. The deposit morphologies obtained for the various Saponin and Sb combinations are similar to that shown in Figure 15. The deposit consists of distinct, relatively uniform nodules which are composed of well-defined hexagonal zinc platelets aligned at intermediate angles to the Al cathode.

Antimony and Sodium Silicate

The effect of increasing Sb concentration with 45 mg/L Na_2SiO_3 on the CE, NOP and orientation for 6-h zinc deposits is shown in Table 9. The addition of 0.005 or 0.01 mg/L Sb

increases the CE, changes the deposit orientation from [103][002][102][114][101] to [101][201][112], but decreases both the initial and final NOP values. The deposit surface remains nodular with circular pits, Figure 16(a). For Sb >0.01 mg/L, the CE decreases, the deposit orientation becomes basal and the NOP values continue to decrease. The deposit morphology, shown in Figure 16(b), consists of stacks of platelets with rounded edges, indicating that zinc re-solution occurs under these conditions. Figure 17 compares the CE vs Sb concentration with and without the presence of 45 mg/L Na_2SiO_3. The decrease in CE with increasing Sb is greater in the presence of Na_2SiO_3 particularly when the Sb concentration is >0.02 mg/L.

Antimony, Dowfroth and Saponin

It has been shown that the alternative foaming agent, Saponin, is less polarizing than Dowfroth. Like Dowfroth, however, Saponin has a beneficial interaction with low concentrations of antimony. These results suggested that the Dowfroth concentration of the electroyte could be reduced to minimize its effect on zinc deposition polarization and that the quality of the foam layer on the electrolyte could be maintained by the addition of Saponin. In this regard, the CE, orientation and NOP data obtained for various combinations of Dowfroth + Saponin + Sb are presented in Table 10. The Saponin concentrations were 1, 3, 5 and 10 mg/L at fixed levels of Dowfroth + Sb; i.e., 3 mg/L Dowfroth + 0.02 mg/L Sb. In general,

aponin additions had no effect on the CE although there appears o be an increase in the CE at all Dowfroth + Sb combinations ten the Saponin concentration is 3 mg/L. At 3 mg/L Dowfroth + mg/L Saponin, increasing Sb to 0.01 mg/L resulted in an ncrease in CE; at 7 mg/L Dowfroth + 3 mg/L Saponin increasing Sb o 0.015 mg/L did not significantly change the CE. The preferred posit orientation was [101][112] for 3 and 10 mg/L Dowfroth th various Sb + Saponin concentrations, but was [101] for mg/L Dowfroth with Sb + Saponin, Table 10. No consistent rends were noted for the initial and final NOP values. For wfroth >3 mg/L, the addition of 1 mg/L Saponin lowers both the nitial and final NOP values; the NOP values then begin to crease with increasing Saponin concentration, Table 10.

The deposit morphologies obtained for 3 mg/L Dowfroth + mg/L Saponin + 0.005 mg/L Sb and for 7 mg/L Dowfroth + 3 mg/L aponin + 0.01 mg/L Sb are shown in Figures 18(a) and 18(b), espectively.

Antimony, Dowfroth, Saponin and Sodium Silicate

The CE, orientation and NOP data obtained for various mbinations of Dowfroth, Saponin and Sb with 45 mg/L Na_2SiO_3 are resented in Table 11. For the 3 mg/L Dowfroth series, the resence of 45 mg/L Na_2SiO_3 resulted in a slight increase in the E values whereas for the 7 and 10 mg/L Dowfroth series, the CE's ecreased, cf. Tables 10 and 11. The preferred orientations emained unchanged with the addition of 45 mg/L Na_2SiO_3 except

for the solutions containing 10 mg/L Dowfroth when the orientations became [101], cf., Tables 10 and 11. The presence of 45 mg/L Na_2SiO_3 seems to improve the deposit morphology, Figs. 19(a) and 19(b).

24-h Confirmation Tests

A series of 24-h tests was done to confirm the antimony, Dowfroth, Saponin and sodium silicate effects observed for the 6-h tests described above. The results obtained for selected combinations of these reagents on the CE, orientation, nucleation overpotential and Pb content of 24-h zinc deposits are presented in Table 12. Increasing Sb from 0.01 to 0.015 mg/L in an electrolyte containing 3 mg/L Dowfroth results in a small increase in CE but does not change the preferred orientation or the final NOP, Table 12. The addition of 1 or 3 mg/L Saponin to an electrolyte containing 3 mg/L Dowfroth + 0.01 mg/L Sb results in a small decrease in the CE but does not significantly alter the preferred orientation or the final NOP. The addition of 45 mg/L Na_2SiO_3 to an electrolyte containing 3 mg/L Dowfroth + 0.01 mg/L Sb and 1 or 3 mg/L Saponin essentially raises the CE back to that obtained for 3 mg/L Dowfroth + 0.01 mg/L Sb. In the same solution, reducing the Sb concentration from 0.01 to 0.005 mg/L lowers the CE and raises the final NOP value, but increasing Saponin to 3 mg/L increases the CE, Table 12.

At 7 mg/L Dowfroth + 0.015 mg/L Sb the addition of 1 or 3 mg/L Saponin did not affect significantly the CE; the preferred orientation remained [101], Table 12. The addition of 45 mg/L Na_2SiO_3 to an electrolyte containing 7 mg/L Dowfroth + 0.015 mg/L Sb + 1 mg/L Saponin slightly increased the CE; however, reducing the Sb content of this electrolyte to 0.005 mg/L decreased the CE. Raising the Saponin to 3 mg/L, however, again increased the CE.

The deposit morphologies for the 3 and 7 mg/L Dowfroth series are shown in the SE photomicrographs, Figures 20 and 21, respectively. The deposits shown in Figure 20 are compact and nodular; the addition of Saponin results in smaller, more distinct nodules, Figures 20(b) and (c), whereas the addition of 45 mg/L Na_2SiO_3 results in a ridge-like surface, Figure 20(d). At 7 mg/L Dowfroth, the deposit grain size is refined and the nodules disappear but are replaced by long tubular-like ridges, Figure 21. The deposits are all very similar.

A photograph of some of the 24-h zinc deposits electrowon from electrolytes containing either 3 or 7 mg/L Dowfroth with various concentrations of Sb, Saponin and sodium silicate is presented in Figure 22. The vertical striations which occur in the presence of 7 mg/L Dowfroth are clearly visible.

In most cases, the Pb content of the zinc deposits was <20 ppm, Table 12; i.e., well within the Pb specification for special high grade zinc.

The corresponding data for the 6-h and 24-h deposition tests for the various Dowfroth, antimony, Saponin and sodium silicate combinations are compared in Table 13 and show that very good agreement was obtained between the corresponding CE, orientation and final NOP results.

Plant Evaluations

During the course of the laboratory studies at CANMET, Kidd Creek carried out several in plant evaluations of addition agent concentration and of various combinations of addition agents. When this study was initiated, the reagent additions to the Kidd Creek zinc electrolyte were: 7-10 mg/L Dowfroth 250, 0.02 mg/L Sb, 45 mg/L Na_2SiO_3 and either 3 kg $BaCO_3$/ton Zn or 1 kg $SrCO_3$/ton Zn. This additive mix produced quality zinc deposits containing <30 ppm Pb at >90% CE under ideal operating conditions, but was not adequate to handle certain plant upset conditions. For example, Dowfroth, in addition to supressing acid mist, is also a strong polarizing agent which adversely affects the zinc deposit quality and CE if its concentration in the electroyte is not carefully controlled. Dowfroth at 7-10 mg/L, is already at its maximum tolerable limit so that an upset condition requiring more Dowfroth to increase the foam layer would have an adverse effect on zinc deposition CE. Thus, it is desirable to lower the concentration of Dowfroth in the electrolyte while at the same time maintaining an adequate foam layer on the electrolyte. As the current laboratory studies indicated, one means of achieving

this goal is to add some Saponin with a lower concentration of Dowfroth to maintain the desired foam layer thickness. As a result, Kidd Creek has reduced the Dowfroth concentration to 5 mg/L and has introduced Saponin at 1 mg/L for acid mist suppression.

Antimony has been shown to be a very important additive in the Kidd Creek electrolyte. Kidd Creek has lowered the Sb concentration from 0.02 to 0.015 mg/L, but of equal importance, the method of Sb addition has been modified to ensure closer control of the desired concentration. Thus, the potassium antimony tartrate is now dried and repackaged as one pound units prior to addition to the electrolyte.

The role of sodium silicate in the Kidd Creek additive scheme has not yet been determined. The laboratory work showed that the 45 mg/L Na_2SiO_3 concentration normally added to the electrolyte slightly improved zinc deposition. During the present plant evaluation of reagent additions, however, the concentration of Na_2SiO_3 has been gradually reduced to 13 mg/L with no adverse effects. Furthermore, the lead content of the zinc deposits is maintained at about 10 ppm by adding 50-100 mg/L strontium. The deposit morphology obtained for the current mix of addition reagents; viz., 5 mg/L Dowfroth 250, 1 mg/L Saponin, 0.015 mg/L Sb, 13 mg/L sodium silicate and 50-100 mg/L strontium is shown in the series of SE micrographs, Figure 23. The deposit consists of uniform nodules composed of zinc platelets aligned at intermediate angles to the Al cathode resulting in a [101][112]

preferred orientation. The CE was 92.2% and the Pb content of the deposit was 13 ppm. These results are in excellent agreement with those obtained for the 24-h laboratory confirmation tests described in this report.

CONCLUSIONS

The individual and combined effects of antimony, Dowfroth 250, Saponin and sodium silicate on zinc electrowinning from Kidd Creek electrolyte were determined in 6-h electrolysis tests conducted at 500 A/m^2 current density and 38°C. At concentrations <0.02 mg/L, antimony increased the current efficiency and improved the deposit quality; at >0.02 mg/L, antimony depolarized zinc deposition, decreased the current efficiency and produced a zinc deposit having a preferred basal orientation. Sodium silicate had no effect on the current efficiency, but high sodium silicate concentrations resulted in a deposit surface containing numerous circular depressions.

The foaming agents, Dowfroth and Saponin decreased the zinc deposition current efficiency. Dowfroth was confirmed to be a strong polarizing agent that significantly reduced the zinc deposit grain size and yielded a zinc deposit having a strongly preferred [101] orientation. Saponin, however, although modifying the deposit morphology, was a weak polarizing reagent and did not alter significantly the deposit orientation.

Both Dowfroth and Saponin had a positive interaction with low concentrations of antimony such that certain combinations of these reagents with antimony maximized the current efficiency. Sodium silicate, however, had a negative interaction with antimony such that the decrease in current efficiency with increasing antimony concentration was accelerated in the presence of sodium silicate. Saponin concentrations to 10 mg/L combined with optimum Dowfroth and antimony additions did not change significantly the current efficiency or deposit characteristics. At optimum concentrations of Dowfroth, Saponin and antimony, the addition of sodium silicate resulted in a small increase in current efficiency (<1%) but did not change the deposit characteristics.

Confirmatory 24-h electrolysis tests using selected combinations of the reagents were done employing Pb-Ag anodes and strontium carbonate additions to simulate plant practice. The results obtained were in excellent agreement with the 6-h test data and the zinc deposits contained <30 ppm Pb; i.e., they were special high grade zinc quality. The results obtained for this phase of the laboratory study suggest that the range of reagent addition concentrations should be set as follows: antimony at 0.01 to 0.015 mg/L, Saponin at 1-3 mg/L, and Dowfroth at 3-7 mg/L. The need for sodium silicate has yet to be conclusively demonstrated.

Plant evaluation tests were carried out simultaneously with the laboratory studies. These tests involved reducing the

Dowfroth concentration and adding low levels of Saponin to maintain an adequate foam layer on the electrolyte surface. The antimony concentration also was reduced, and the method of adding the antimony to the cells was modified to allow a more precise control of its concentration in the electrolyte. The concentration of sodium silicate was also reduced. As a result of these adjustments, the reagent addition mix to the Kidd Creek zinc electrolyte comprises the following: 5 mg/L Dowfroth 250, 1 mg/L Saponin, 0.015 mg/L Sb and 13 mg/L Na_2SiO_3 with 50 to 100 mg/L Sr for Pb control. The resulting deposit characteristics are in excellent agreement with those obtained for the 24-h laboratory confirmation tests.

ACKNOWLEDGEMENTS

Thanks are due to P. Carriere of CANMET for doing the X-ray diffraction analyses and to the Kidd Creek Division of Falconbridge Limited for supplying the electrolyte, addition reagents and electrode materials and for permission to publish this work.

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Table 1. Analyses of Neutral and Cold Spent Solutions Received from Kidd Creek

Analyte	Neutral Solution	Cold Spent Solution
Mg (g/L)	2.3 - 2.5	2.5 - 2.8
Mn (g/L)	9.7 - 10.4	9.5 - 10.5
Na (g/L)	2.8 - 3.0	2.7 - 2.9
S (g/L)	100.7 - 107.9	105.9 - 116.9
Zn (g/L)	186.5 - 200.6	57.9 - 64.0
H_2SO_4 (g/L)	-	196.0 - 208.0
Ag (mg/L)	1	1
Al (mg/L)	16 - 20	28
As (mg/L)	<0.01	0.03
Sb (mg/L)	<0.01	<0.01
Se (mg/L)	<0.05	<0.05
Sn (mg/L)	<0.2	<0.2
Ba (mg/L)	0.6	1
Ca (mg/L)	305 - 350	309 - 313
Cd (mg/L)	0.6	<0.1
Co (mg/L)	0.2	0.3
Cr (mg/L)	<0.1	<0.1
Cu (mg/L)	0.1 - 0.3	0.1
Fe (mg/L)	16 - 20	15
Ga (mg/L)	<1	<1
In (mg/L)	<1	<1
Ni (mg/L)	<1	<1
Pb (mg/L)	1	1
Si (mg/L)	225 - 240	88 - 94

Table 2. The Effect of Antimony on the Current Efficiency, Orientation and Nucleation Overpotential for 6-h Zinc Deposits Electrowon at 500 A/m^2 and 38°C

Sb (mg/L)	CE (%)	ORIENTATION[1]	NOP (mV) (Initial)	(Final)
0	90.7	114,112,103,102,101	120	145
0.005	90.8	114,112,103,102,101	105	150
0.01	92.9	101,112	110	130
0.015	93.3	101,201	85	135
0.02	90.8	114,112,103,102,101	60	90
0.025	85.3	114,103,112,102,101	65	120
0.03	86.7	112,114,103,102,101	60	120
0.04	85.6	105,103,114	50	92
0.06	77.9	105,103,114,102,112	60	87
0.08	29.0	-------	55	85

[1] Relative to ASTM Standard for zinc powder.

Table 3. The Effect of Dowfroth on the Current Efficiency, Orientation and Nucleation Overpotential for 6-h Zinc Deposits Electrowon at 500 A/m^2 and 38°C

Dowfroth (mg/L)	CE (%)	ORIENTATION[1]	NOP (mV) (Initial)	(Final)
0	90.7	114,112,103,102,101	120	145
3	87.6	112,103,102,114,101	150	150
7	88.0	101	140	155
10	87.5	101	155	145
15	86.2	101	140	140
20	85.4	101	170	160
25	84.9	101	190	155
30	83.6	101	175	150
40	83.3	101	190	145
50	82.0	101	210	145
75	81.2	101	230	150

[1] Relative to ASTM Standard for zinc powder.

Table 4. The Effect of Saponin on the Current Efficiency, Orientation and Nucleation Overpotential for 6-h Zinc Deposits Electrowon at 500 A/m^2 and 38°C

Saponin (mg/L)	CE (%)	ORIENTATION[1]	NOP (mV) (Initial)	(Final)
0	90.7	114,112,103,102,101	120	145
1	89.3	114,103,112,102,101	140	150
3	89.7	114,103,112,102,101	155	155
5	88.4	114,112,103,102,101	153	150
10	88.1	114,112,103,102,101	135	140
15	89.2	112,102,103,114,101	140	130
20	89.6	112,114,103,101	140	140
25	90.3	112,114,101	150	135
30	89.5	112,114,103,201,101	150	135
40	89.0	114,201,112,110,103,101	160	145
50	89.2	114,110,201,110,002,112,101	150	150
75	88.1	002,100,110,114,112,101	165	155
100	86.0	100,110,002,201	165	155
1000	77.1	110,100,002,201	190	145

[1] Relative to ASTM Standard for zinc powder.

Table 5. The Effect of Sodium Silicate on the Current Efficiency, Orientation and Nucleation Overpotential for 6-h Zinc Deposits Electrowon at 500 A/m^2 and 38°C

Sodium Silicate (mg/L)	CE (%)	ORIENTATION[1]	NOP (mV) (Initial)	(Final)
0	90.7	114,112,103,102,101	120	145
15	90.3	114,112,103,102,101	140	130
45	90.1	103,002,102,114,101	135	150
90	90.6	114,112,103,102,101	140	160
270	91.2	103,002,102,114,101	150	160
450	90.8	112,114,103,102,101	160	150

[1] Relative to ASTM Standard for zinc powder.

Table 6. The Effect of Antimony and Dowfroth on the Current Efficiency, Orientation and Nucleation Overpotential for 6-h Zinc Deposits Electrowon at 500 A/m^2 and 38°C

Sb (mg/L)	Dowfroth (mg/L)	CE (%)	ORIENTATION[1]	NOP (mV) (Initial)	(Final)
0	3	87.6	112,103,102,114,101	150	150
0.005	3	91.8	101,112	120	140
0.010	3	92.3	101,112	100	130
0.015	3	91.8	101,112	105	130
0.020	3	91.4	101,112	110	135
0	7	88.0	101	140	155
0.005	7	89.4	101	130	140
0.010	7	89.7	101	140	155
0.015	7	91.5	101,112	115	125
0.020	7	91.1	101,112	130	150
0	10	87.5	101	155	145
0.005	10	87.5	101	160	135
0.010	10	88.7	101	155	145
0.015	10	88.4	101	145	145
0.020	10	91.7	101	130	140
0	15	86.2	101	155	130
0.005	15	88.2	101	150	150
0.010	15	88.5	101	145	145
0.015	15	88.6	101	140	140
0.020	15	90.0	101	140	140

[1] Relative to ASTM Standard for zinc powder.

Table 7. Current Efficiency, Orientation and NOP Values at Optimum Dowfroth + Antimony Concentrations

Dowfroth (mg/L)	Sb (mg/L)	ORIENTATION[1]	CE (%)	NOP (mV) (Initial)	(Final)
3	0.010	101,112	92.3	100	130
7	0.015	101,112	91.5	115	125
10	0.020	101	91.7	130	140
15	0.020	101	90.0	140	140

[1] Relative to ASTM Standard for zinc powder.

Table 8. The Effect of Antimony and Saponin on the Current Efficiency, Orientation and Nucleation Overpotential for 6-h Zinc Deposits Electrowon at 500 A/m^2 and 38°C

Sb (mg/L)	Saponin (mg/L)	CE (%)	ORIENTATION[1]	NOP (mV) (Initial)	(Final)
0	1	90.5	114,103,112,102,101	143	145
0.005	1	93.1	101,112	110	135
0.010	1	92.8	101,112	100	135
0.020	1	91.2	112,101,102,103,114	80	120
0.030	1	87.7	112,114,103,102,101	85	125
0	3	90.5	114,103,112,102,101	145	143
0.005	3	92.1	101,112	115	130
0.010	3	93.9	101,112	100	135
0.020	3	91.2	101,112	80	110
0.030	3	89.7	114,112,103,102,101	85	125
0	5	89.4	114,112,103,102,101	153	147
0.005	5	93.5	101,112	125	130
0.010	5	93.5	101,112	95	130
0.020	5	93.1	112,101	95	135
0.030	5	89.7	112,114,103,102,101	80	120
0	10	88.1	114,112,103,102,101	135	140
0.005	10	92.6	101,112	125	135
0.010	10	93.1	114,112,101	110	125
0.020	10	92.6	114,101	85	90
0.030	10	92.5	114,103,112,102,101	85	120

[1] Relative to ASTM Standard for zinc powder.

Table 9. The Effect of Antimony and Sodium Silicate on the Current Efficiency, Orientation and Nucleation Overpotential for 6-h Zinc Deposits Electrowon at 500 A/m^2 and 38°C

Sb (mg/L)	Na_2SiO_3 (mg/L)	CE (%)	ORIENTATION[1]	NOP (mV) (Initial)	(Final)
0	45	90.1	103,002,102,114,101	135	150
0.005	45	93.7	101,201,112	95	140
0.01	45	92.5	112,101	80	130
0.015	45	88.1	114,112,103,102,101	75	125
0.02	45	84.6	114,112,103,102,101	75	115
0.025	45	84.7	114,112,103,102,101	70	125
0.03	45	80.9	103,105,114,102,112	70	125
0.04	45	75.1	103,105,114,102,112	70	125
0.06	45	27.0	-----	70	100

[1] Relative to ASTM Standard for zinc powder.

Table 10. The Effect of Dowfroth, Saponin and Antimony on the CE, Orientation and NOP Values for 6-h Zinc Deposits Electrowon at 500 A/m^2 and 38°C

Dowfroth (mg/L)	Saponin (mg/L)	Sb (mg/L)	CE (%)	ORIENTATION[1]	NOP (mV) (Initial)	(Final)
3	0	0.005	91.8	101,112	120	140
3	1	0.005	90.6	101,112	140	105(?)
3	3	0.005	91.0	101,112	140	120
3	5	0.005	90.1	101,112	130	130
3	10	0.005	90.8	101,112	145	145
3	3	0.01	92.3	101,112	130	150
7	0	0.01	89.7	101	140	155
7	1	0.01	92.0	101	115	115
7	3	0.01	92.7	101	110	120
7	5	0.01	91.3	101	130	125
7	10	0.01	92.1	101	130	135
7	3	0.015	92.3	101	140	145
10	0	0.02	91.7	101	130	140
10	1	0.02	90.8	101,112	125	120
10	3	0.02	92.3	101,112	135	145
10	5	0.02	90.9	101,112	135	145
10	10	0.02	92.1	101,112	140	155

[1] Relative to ASTM Standard for zinc powder.

Table 11. The Effect of Dowfroth, Saponin, Antimony and Sodium Silicate on the Current Efficiency, Orientation and Nucleation Overpotential for 6-h Zinc Deposits at 500 A/m^2 and 38°C

Dowfroth (mg/L)	Saponin (mg/L)	Sb (mg/L)	Na_2SiO_3 (mg/L)	CE (%)	ORIENTATION[1]	NOP (mV) (Initial)	(Final)
3	1	0.005	45	91.9	101,112	110	130
3	3	0.005	45	91.1	101,112	135	130
3	3	0.010	45	91.8	101,112	130	140
3	5	0.005	45	90.8	101,112	135	140
3	10	0.005	45	91.6	101,112	135	145
7	1	0.015	45	93.8	101,112	90	135
7	1	0.010	45	87.5	101	140	130
7	3	0.010	45	87.4	101	145	135
7	3	0.015	45	92.2	101	145	145
7	5	0.010	45	84.8	101	155	135
7	10	0.010	45	89.7	101	125	125
7	5	0.010	45	90.0	101	140	150
10	1	0.02	45	89.8	101	110	130
10	3	0.02	45	90.5	101	130	140
10	5	0.02	45	89.4	101	130	145
10	10	0.02	45	90.2	101	145	145

[1] Relative to ASTM Standard for zinc powder.

Table 12. The Effect of Antimony, Dowfroth, Saponin and Sodium Silicate on the Current Efficiency, Orientation, Nucleation Overpotential and Lead Content of 24-h Zinc Deposits Electrowon at 500 A/m^2 and 38°C

Sb (mg/L)	Dowfroth (mg/L)	Saponin (mg/L)	Na_2SiO_3 (mg/L)	CE (%)	ORIENTATION[1]	NOP (mV) (Initial)	NOP (mV) (Final)	Pb (ppm)
0.010	3	-	-	92.0	101,112	145	130	33
0.015	3	-	-	92.6	101,112	110	130	22
0.010	3	1	-	91.4	112,101,201	150	125	16
0.010	3	3	-	91.5	101,112	155	130	12
0.010	3	1	45	91.9	101,112	125	120	6
0.010	3	3	45	92.0	101,112	85	110	
0.005	3	1	45	90.5	112,101,114	125	135	8
0.005	3	3	45	91.5	112,101	125	130	12
0.015	7	-	-	90.0	101	140	115	<6
0.015	7	1	-	89.9	101	125	135	11
0.015	7	3	-	90.0	101	135	140	8
0.015	7	1	45	90.9	101	130	120	22
0.005	7	1	45	89.1	101	135	135	<6
0.005	7	3	45	89.9	101	135	140	<6

[1] Relative to ASTM Standard for zinc powder.

Table 13. Comparative data for 6-h and 24-h Zn Deposition - Dowfroth, Saponin, Antimony and Sodium Silicate Series

Dowfroth (mg/L)	Sb (mg/L)	Saponin (mg/L)	Na_2SiO_3 (mg/L)	6-h Deposition CE (%)	6-h Deposition ORIENTATION	6-h Deposition Final NOP (mV)	24-h Deposition CE (%)	24-h Deposition ORIENTATION[1]	24-h Deposition Final NOP (mV)	Pb (ppm)
3	0.01	-	-	92.3	101, 112	130	92.0	101, 112	130	33
3	0.015	-	-	91.8	101, 112	130	92.6	101, 112	130	22
3	0.01	1	-	-	-	-	91.4	112, 101, 201	125	16
3	0.01	3	-	92.3	101, 112	150	91.5	101, 112	120	12
3	0.01	1	45	-	-	-	91.9	101, 112	120	6
3	0.005	1	45	91.9	101, 112	130	90.5	112, 101, 114	135	8
3	0.005	3	45	92.1	101, 112	130	91.5	112, 101	130	12
7	0.015	1	-	-	-	-	89.8	101	135	11
7	0.015	3	-	92.3	101	145	90.4	101	140	8
7	0.015	-	-	91.5	101	125	90.0	101	115	<6
7	0.015	1	45	93.8	101, 112	135	90.9	101	120	22
7	0.005	1	45	-	-	-	89.1	101	135	<6
7	0.005	3	45	-	-	-	89.9	101	140	<6

[1] Relative to ASTM standard for zinc powder

FIGURE CAPTIONS

Figure 1 - Typical cyclic voltammogram for addition-free Kidd Creek zinc electrolyte.

Figure 2 - Plot of current efficiency vs antimony concentration.

Figure 3 - SE micrographs showing the effect of various antimony concentrations on the morphology of 6-h zinc deposits electrowon at 500 A/m^2 and 38°C.

Figure 4 - Plots of initial and final NOP values vs antimony concentration.

Figure 5 - Plots of current efficiency vs sodium silicate, Saponin and Dowfroth concentrations.

Figure 6 - SE micrographs showing the effect of Dowfroth on the morphology of 6-h zinc deposits electrowon at 500 A/m^2 and 38°C.

Figure 7 - SE micrographs showing the effect of Saponin on the morphology of 6-h zinc deposits electrowon at 500 A/m^2 and 38°C.

Figure 8 - Plots of initial and final NOP values vs Saponin concentration.

Figure 9 - SE micrographs showing the effect of sodium silicate on the morphology of a 6-h zinc deposit electrowon at 500 A/m^2 and 38°C.

Figure 10 - Plots of current efficiency vs antimony concentration at various levels of Dowfroth.

Figure 11 - SE micrographs showing the effect of Dowfroth and antimony on the morphology of 6-h zinc deposits electrowon at 500 A/m^2 and 38°C.

Figure 12 - Plots of initial NOP values vs antimony concentration at various levels of Dowfroth.

Figure 13 - Plots of final NOP values vs antimony concentration at various levels of Dowfroth.

Figure 14 - Plots of current efficiency vs antimony concentration at various levels of Saponin.

Figure 15 - SE micrographs showing the effect of Saponin and antimony on the morphology of a 6-h zinc deposit electrowon at 500 A/m^2 and 38°C.

Figure 16 - SE micrographs showing the effect of sodium silicate and antimony on the morphology of 6-h zinc deposits electrowon at 500 A/m^2 and 38°C.

Figure 17 - Plots of current efficiency vs antimony concentration in the presence and absence of sodium silicate.

Figure 18 - SE micrographs showing the combined effects of Dowfroth, Saponin and antimony on the morphology of 6-h zinc deposits electrowon at 500 A/m^2 and 38°C.

Figure 19 - SE micrographs showing the combined effect of Dowfroth, Saponin, antimony and sodium silicate on the morphology of 6-h zinc deposits electrowon at 500 A/m^2 and 38°C.

Figure 20 - SE micrographs showing the effect of various combinations of Dowfroth, antimony, Saponin and sodium silicate on the morphology of 24-h zinc deposits electrowon at 500 A/m^2 and 38°C.

Figure 21 - SE micrographs showing the effects of various combinations of Dowfroth, antimony, Saponin and sodium silicate on the morphology of 24-h zinc deposits electrowon at 500 A/m^2 and 38°C.

Figure 22 - Photographs (1X) of various 24-h zinc deposits electrowon at 500 A/m^2 and 38°C.

Figure 23 - SE micrographs showing the morphology of a 24-h Kidd Creek commercial zinc deposit.

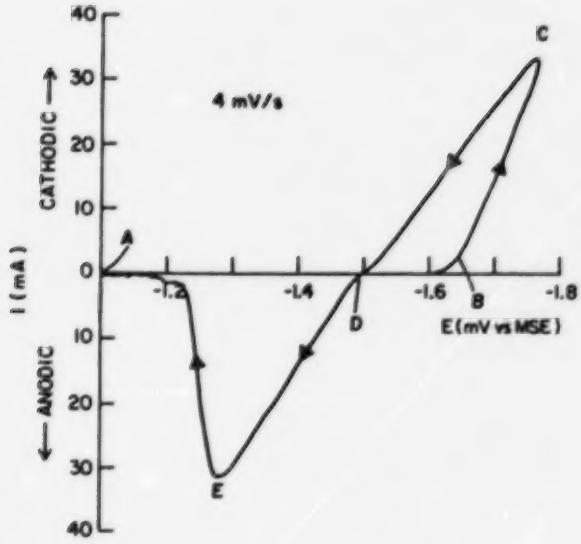


Figure 1. Typical cyclic voltammogram for addition-free Kidd Creek zinc electrolyte.

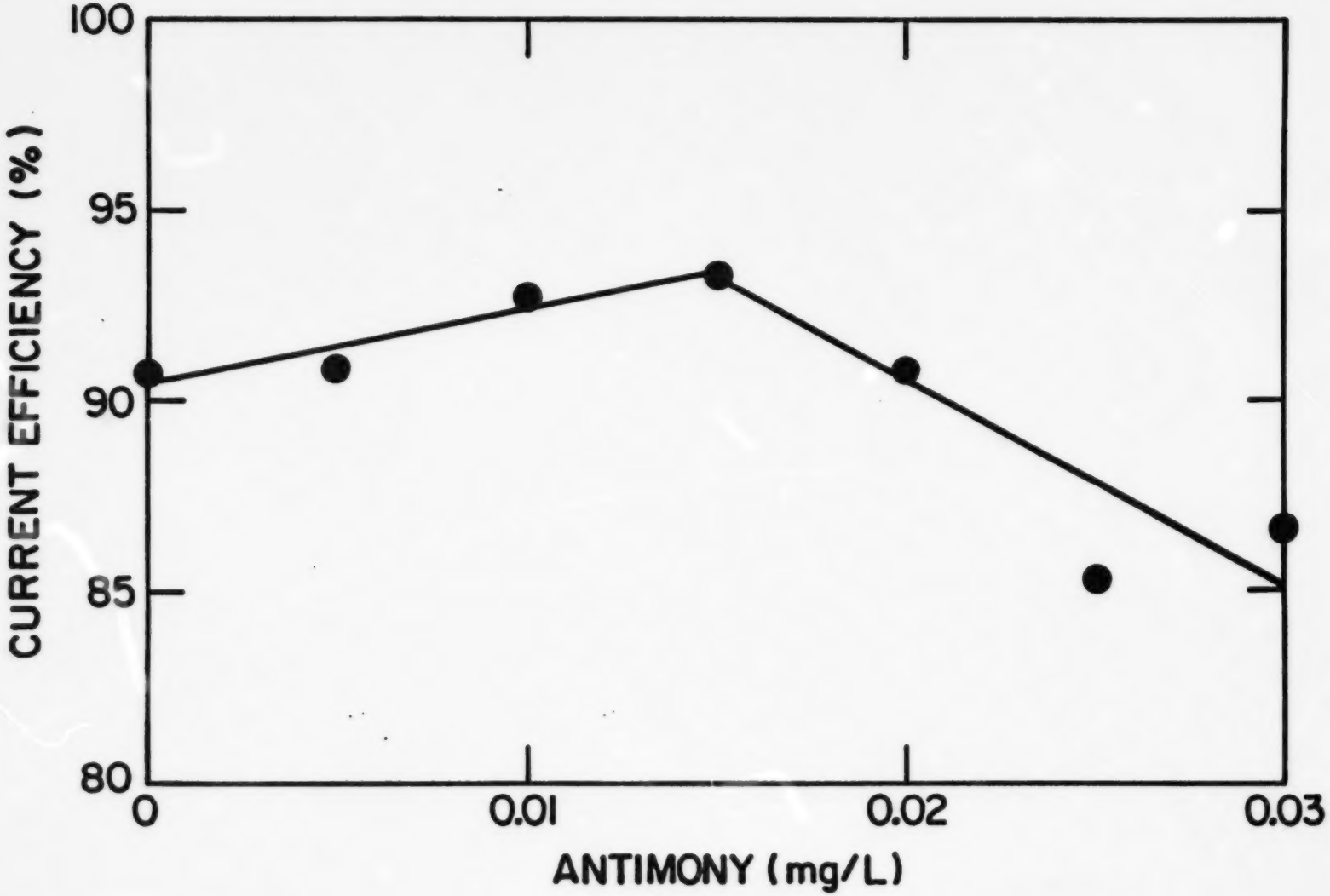
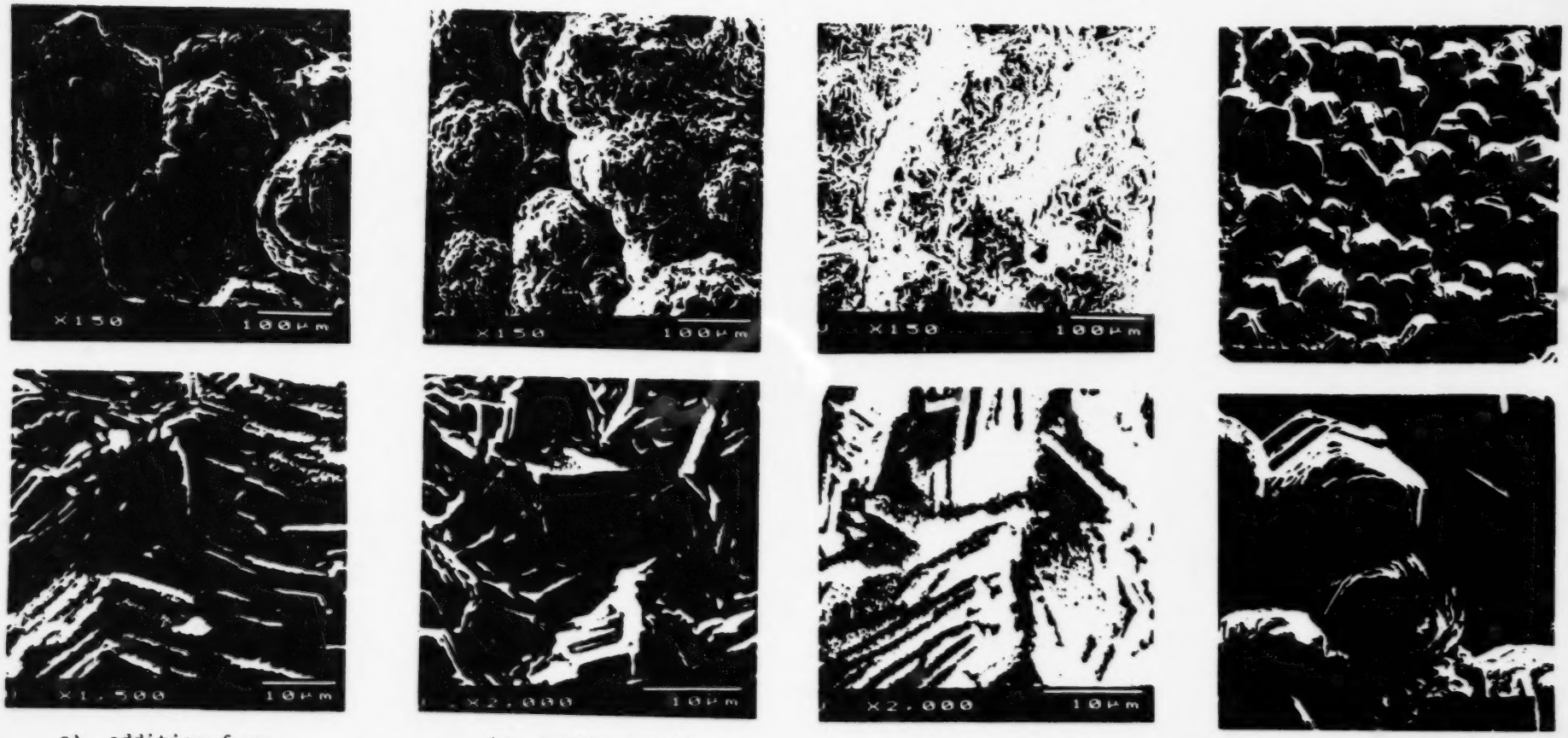


FIG. 2



a) addition-free b) 0.015 mg/L Sb c) 0.03 mg/L Sb d) 0.06 mg/L Sb

Figure 3. SE micrographs showing the effect of various antimony concentrations on the morphology of 6-h zinc deposits electrowon at 500 A/m^2 and 38°C.

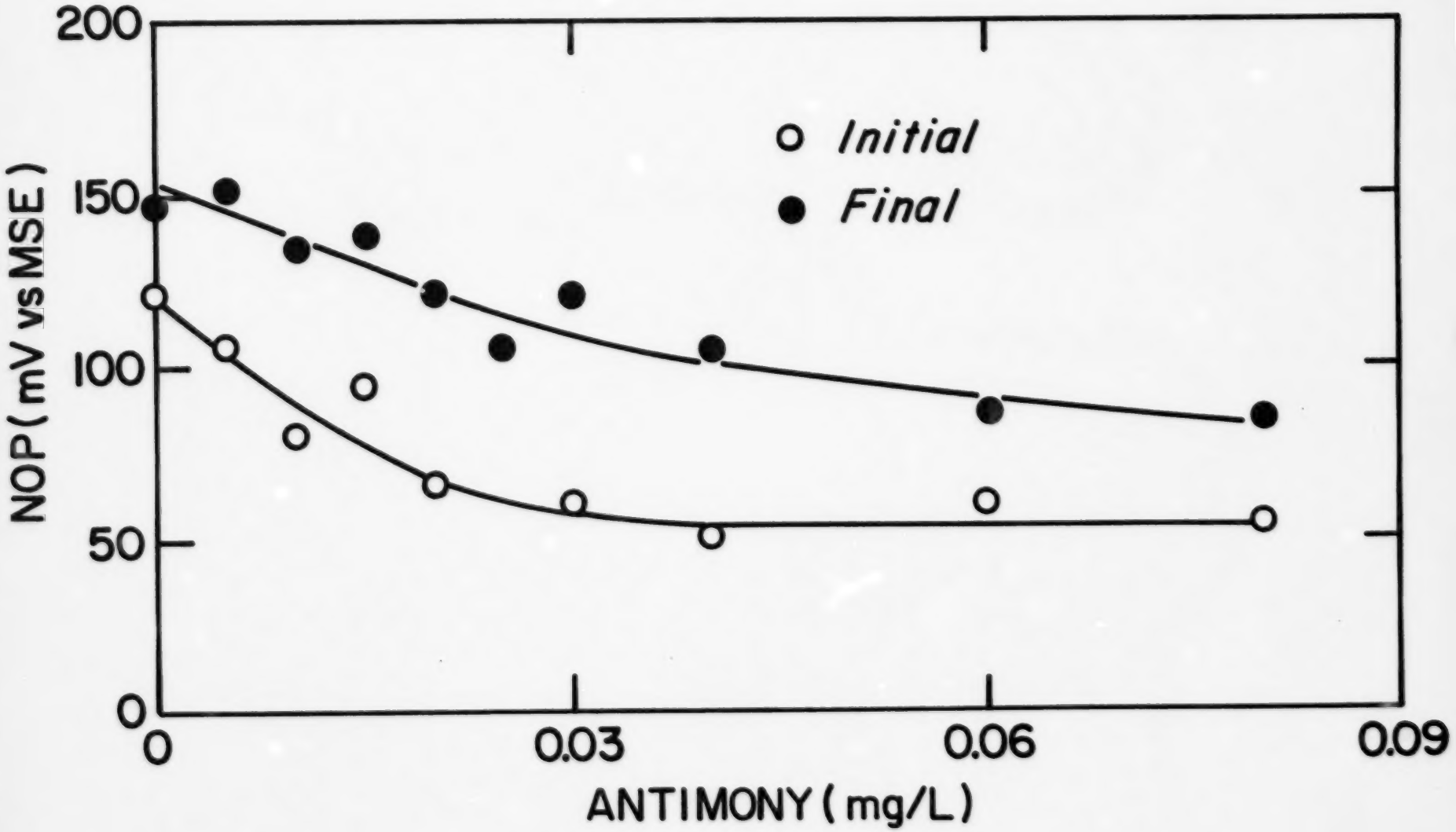

200
150
100
50
0
NOP (mV vs MSE)
Initial
Final
0
0.03
0.06
0.09
ANTIMONY (mg/L)

FIG. 4

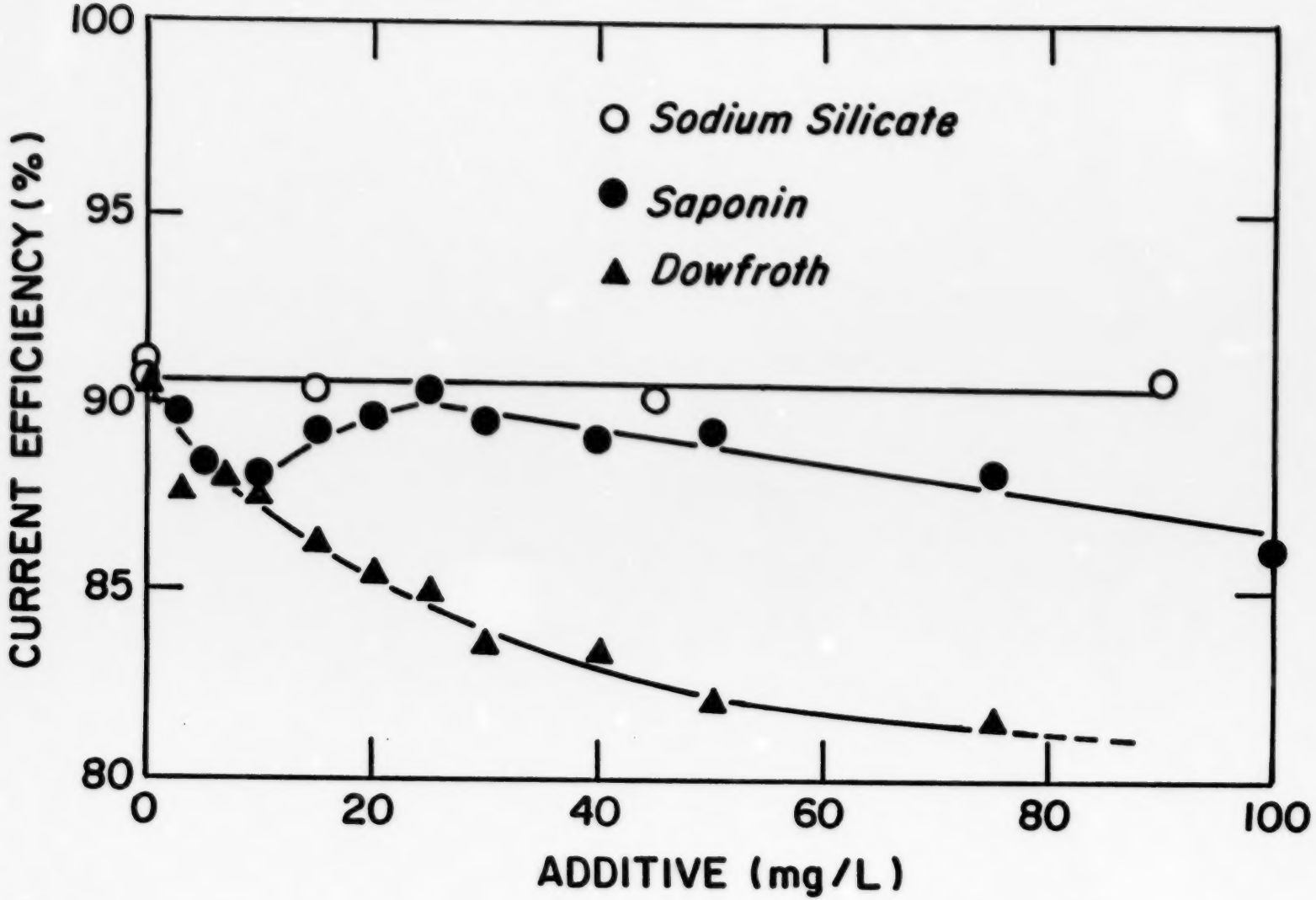
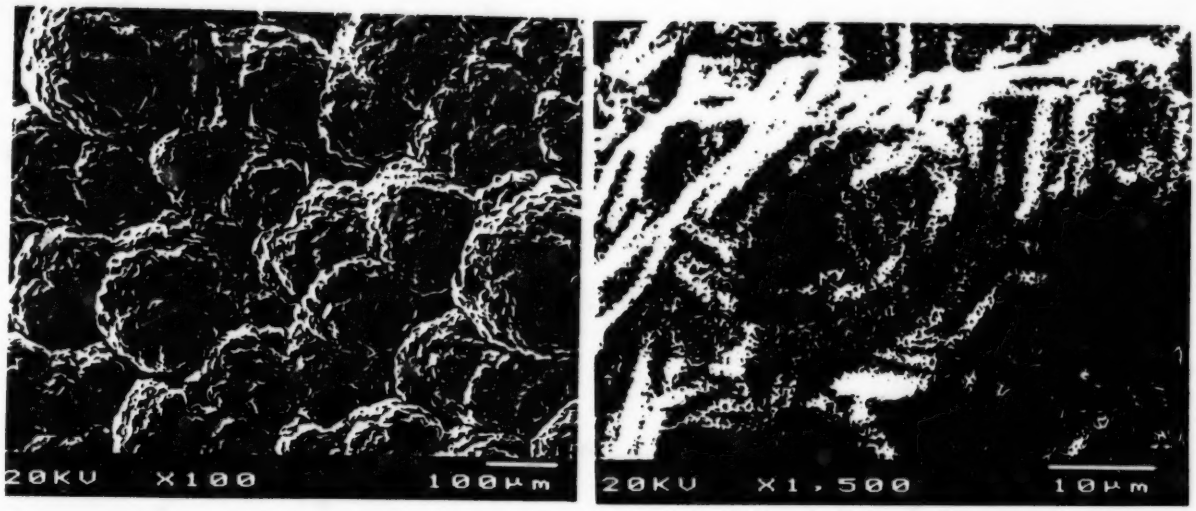
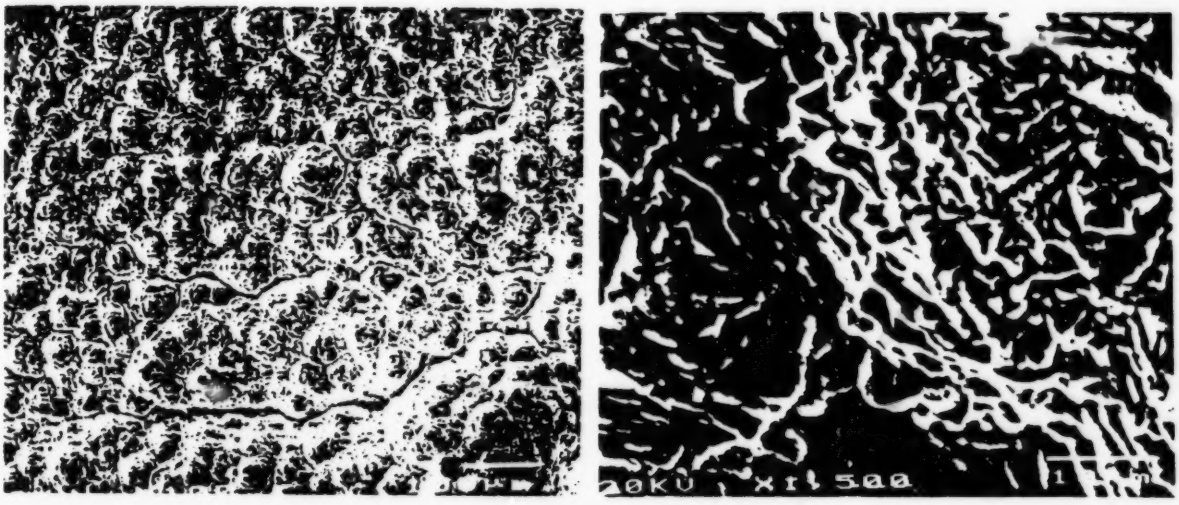

100
95
90
85
80
CURRENT EFFICIENCY (%)
Sodium Silicate
Saponin
Dowfroth
0
20
40
60
80
100
ADDITIVE (mg/L)

FIG. 5

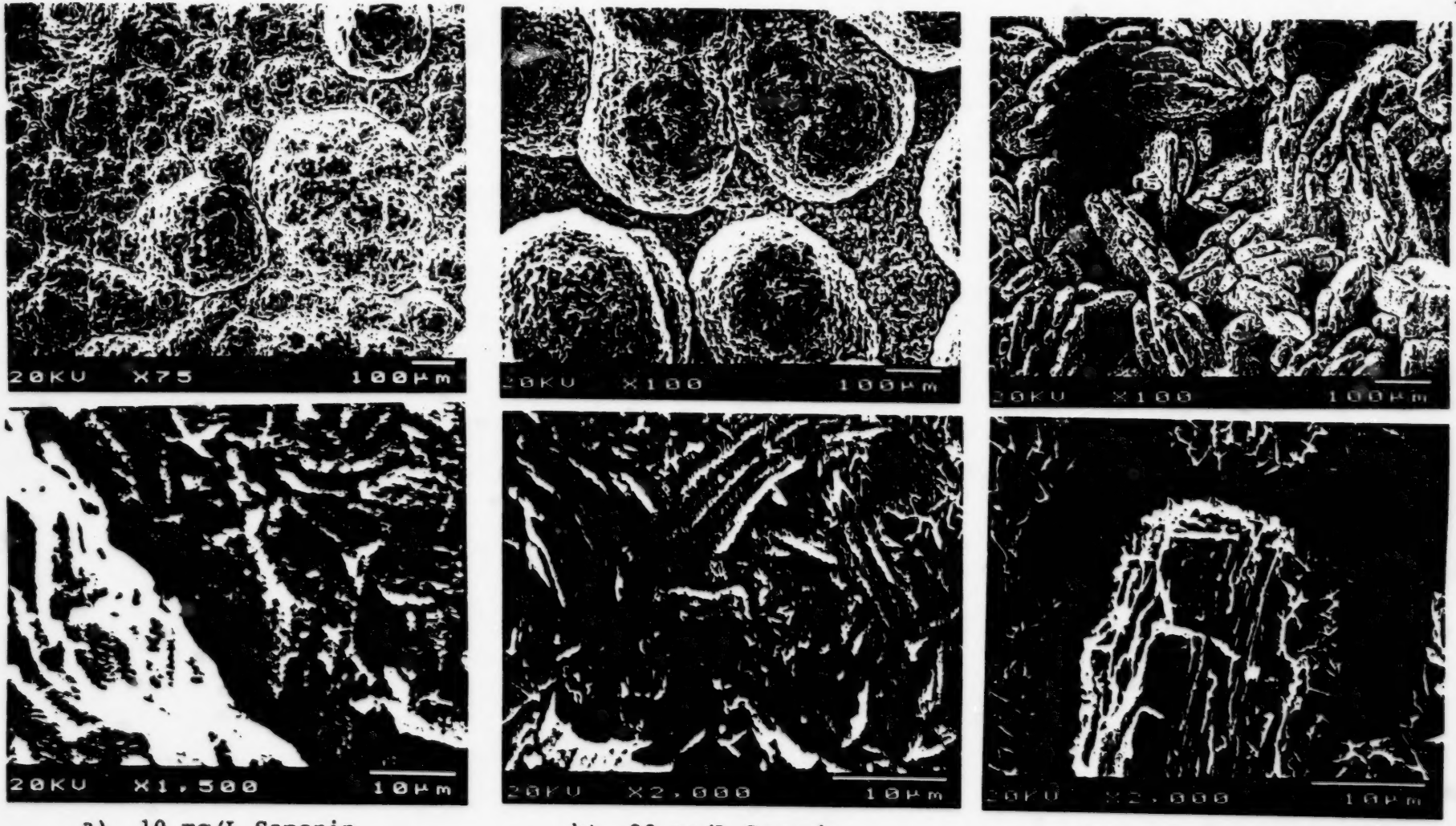


a) 3 mg/L Dowfroth



b) 30 mg/L Dowfroth

Figure 6. SE micrographs showing the effect of Dowfroth on the morphology of 6-h zinc deposits electrowon at 500 A/m^2 and 38°C.



a) 10 mg/L Saponin

b) 20 mg/L Saponin

c) 100 mg/L Saponin

Figure 7. SE micrographs showing the effect of Saponin on the morphology of 6-h zinc deposits electrowon at 500 A/m² and 38°C.

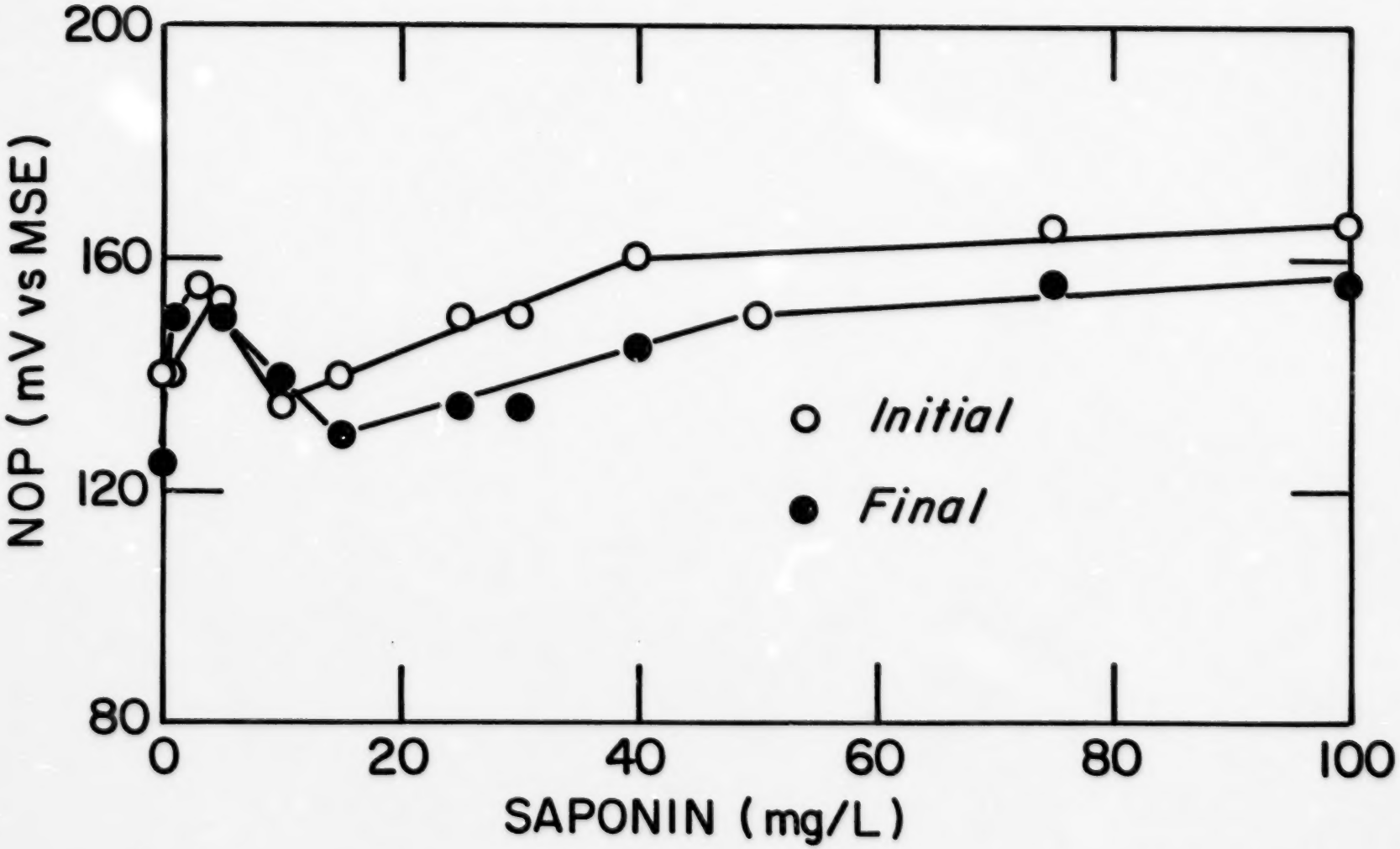
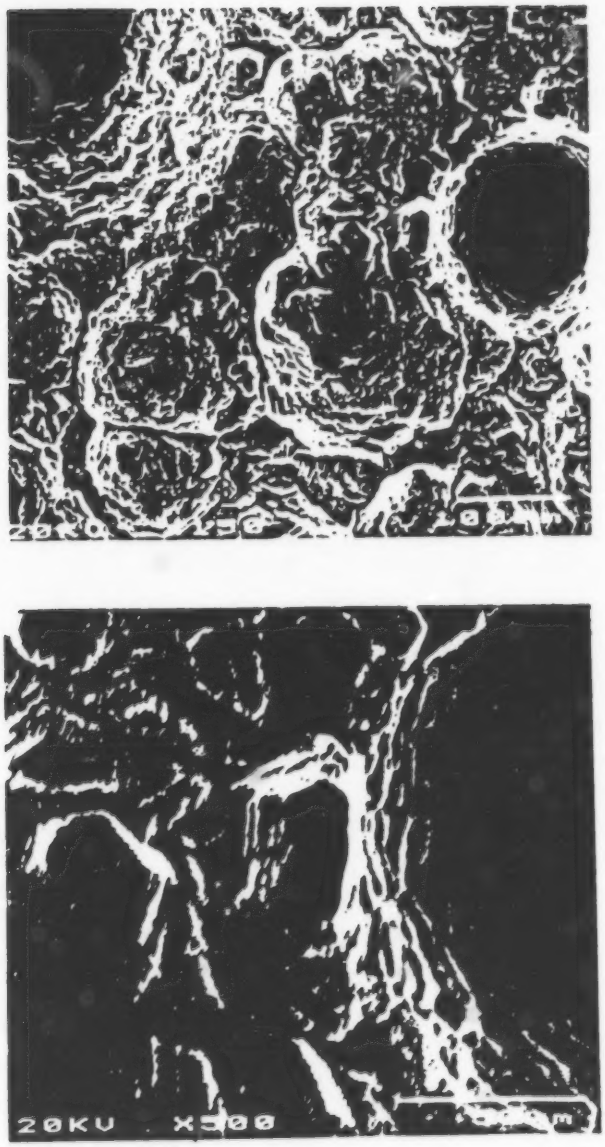

200
160
120
80
NOP (mV vs MSE)
0
20
40
60
80
100
SAPONIN (mg/L)
Initial
Final

FIG. 8



45 mg/L Na_2SiO_3

Figure 9. SE micrographs showing the effect of sodium silicate on the morphology of a 6-h zinc deposit electrowon at 500 A/m^2 and 38°C.

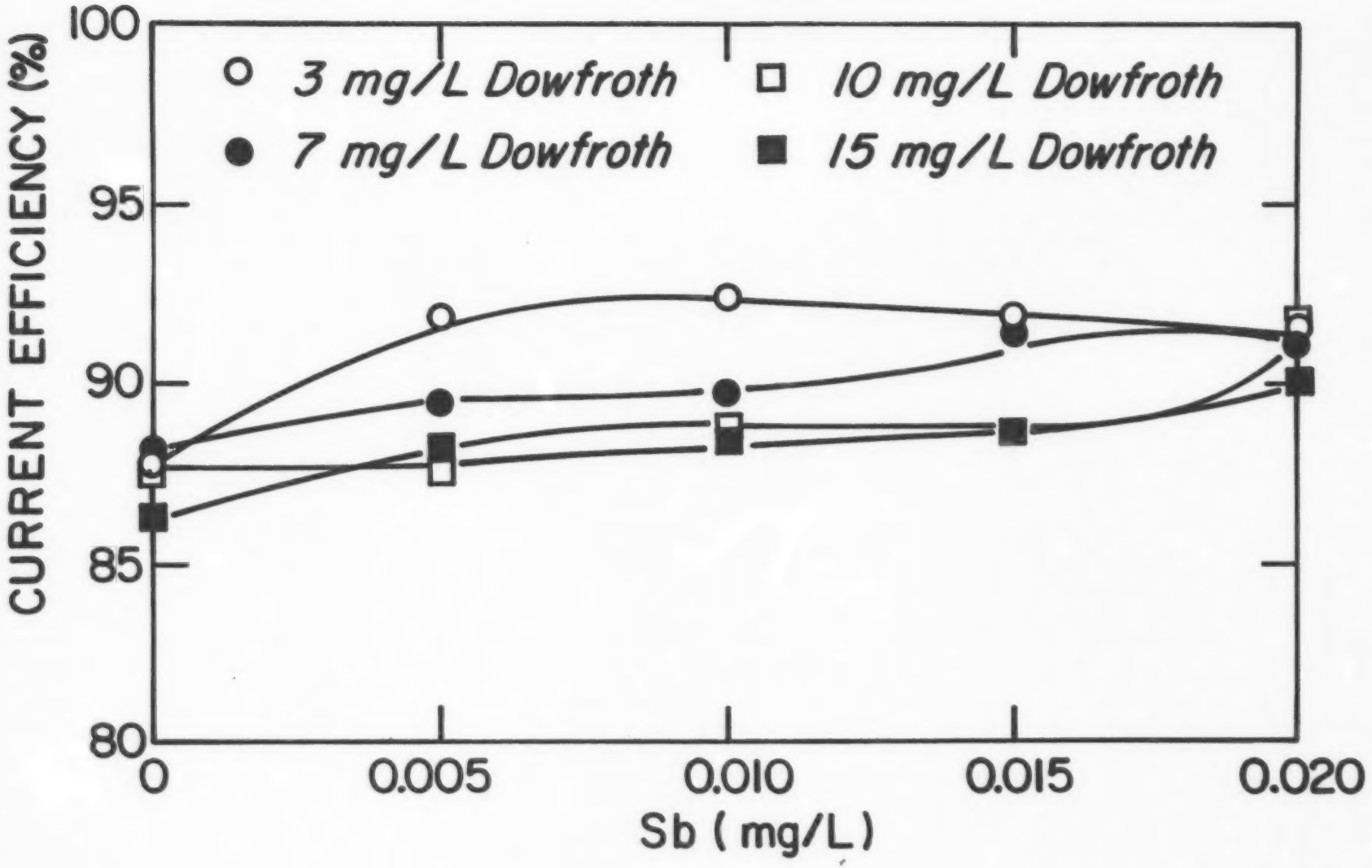
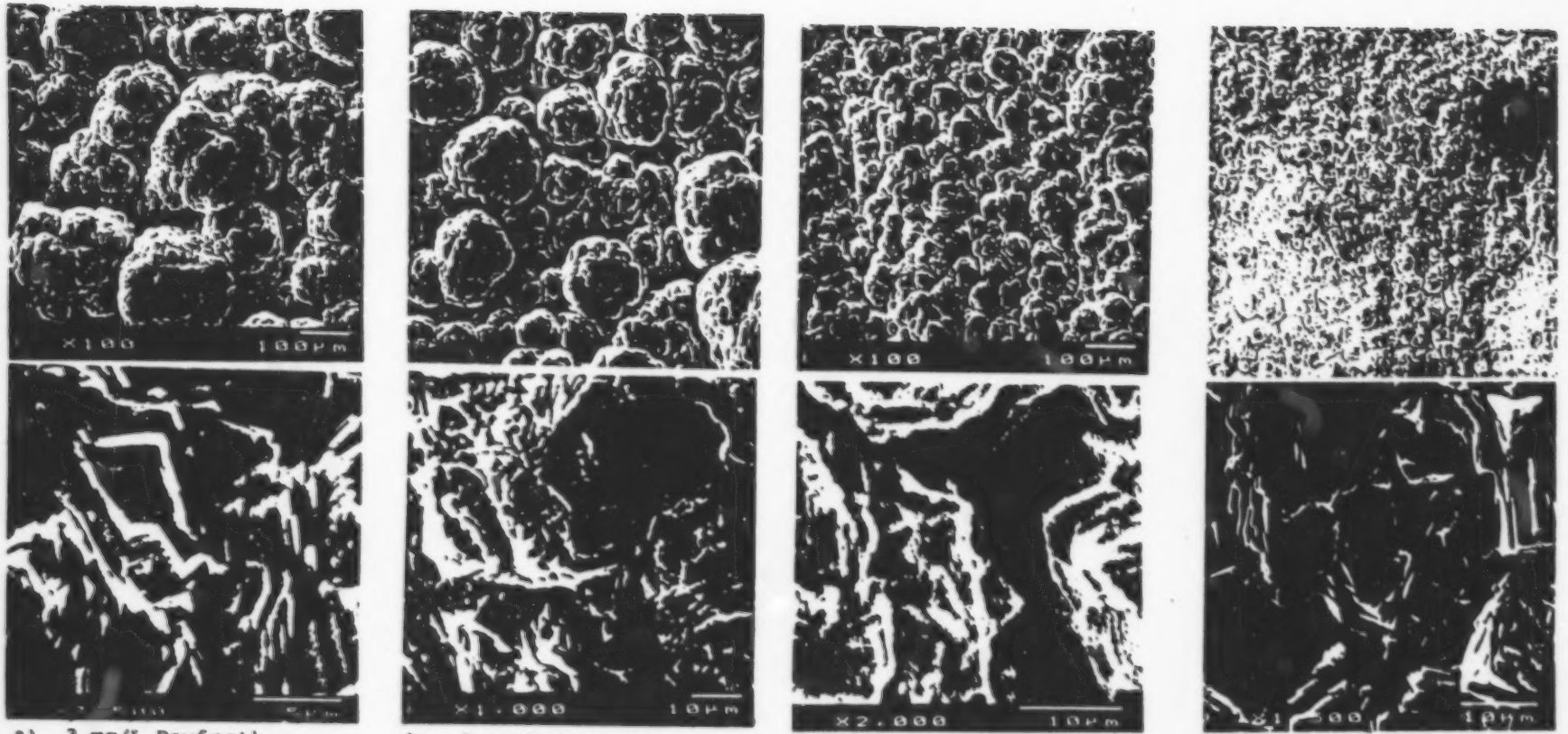

CURRENT EFFICIENCY (%)
100
95
90
85
80
3 mg/L Dowfroth
7 mg/L Dowfroth
10 mg/L Dowfroth
15 mg/L Dowfroth
0
0.005
0.010
0.015
0.020
Sb (mg/L)

FIG. 10



a) 3 mg/L Dowfroth + 0.01 mg/L Sb

b) 7 mg/L Dowfroth + 0.015 mg/L Sb

c) 10 mg/L Dowfroth + 0.02 mg/L Sb

d) 15 mg/L Dowfroth + 0.02 mg/L Sb

Figure 11. SE micrographs showing the effect of Dowfroth and antimony on the morphology of 6-h zinc deposits electrowon at 500 A/m^2 and 38°C.

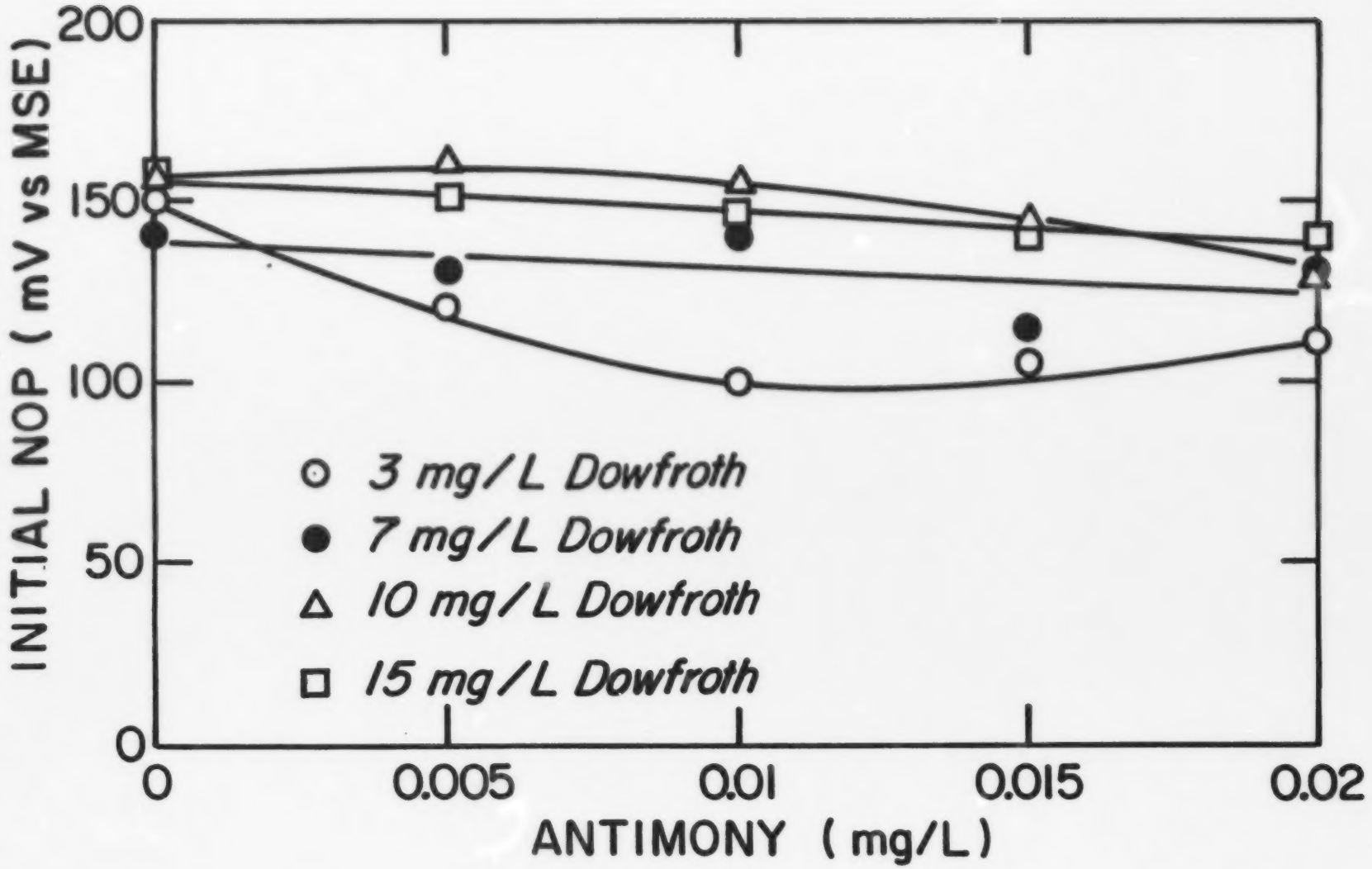

INITIAL NOP (mV vs MSE)
200
150
100
50
0
0
0.005
0.01
0.015
0.02
ANTIMONY (mg/L)
3 mg/L Dowfroth
7 mg/L Dowfroth
10 mg/L Dowfroth
15 mg/L Dowfroth

FIG. 12

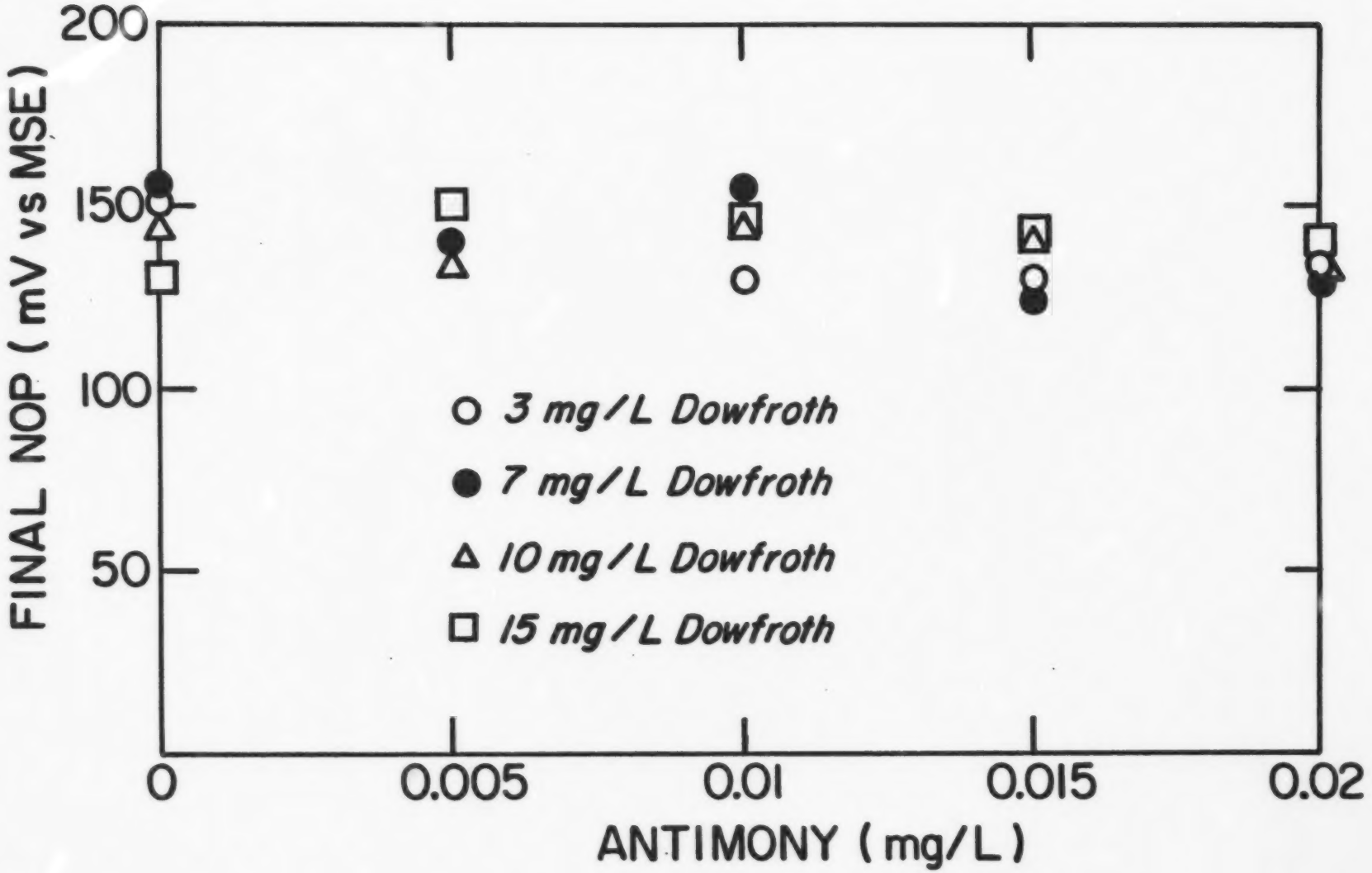

200
150
100
50
FINAL NOP (mV vs MSE)
0
0.005
0.01
0.015
0.02
ANTIMONY (mg/L)
3 mg/L Dowfroth
7 mg/L Dowfroth
10 mg/L Dowfroth
15 mg/L Dowfroth

FIG. 13

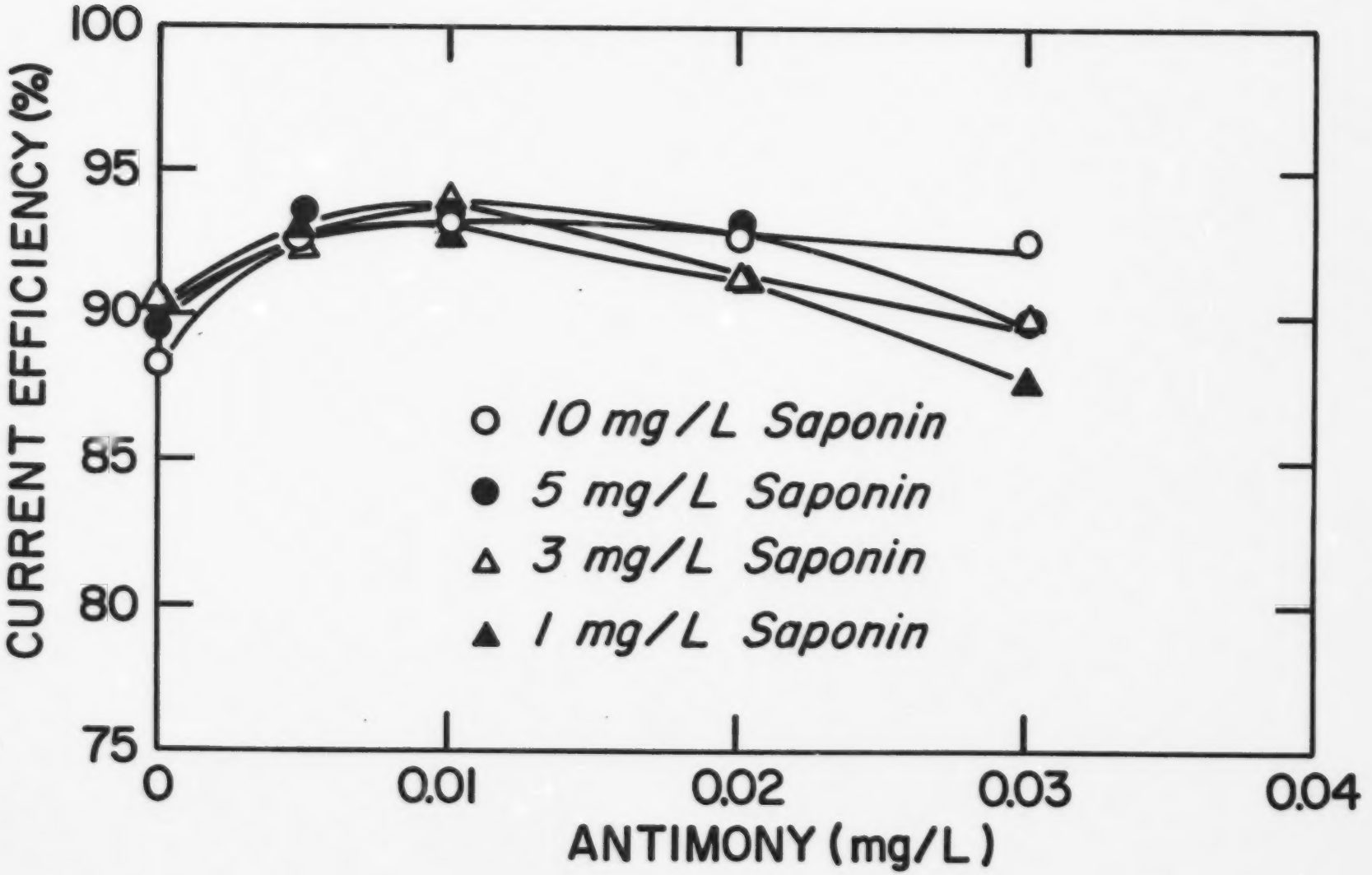
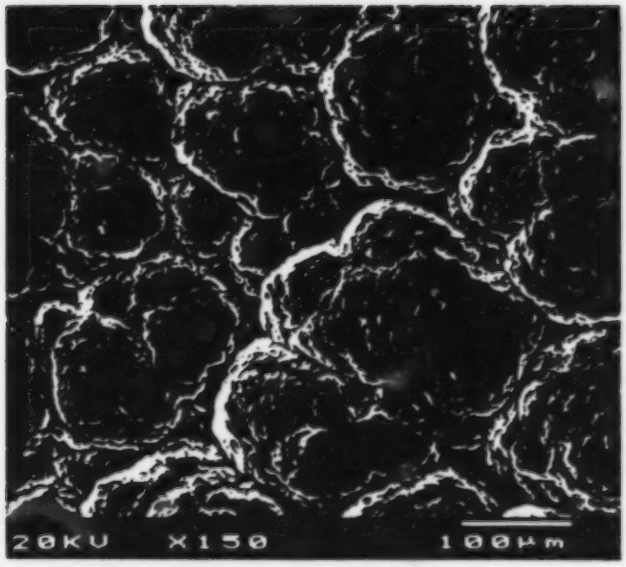
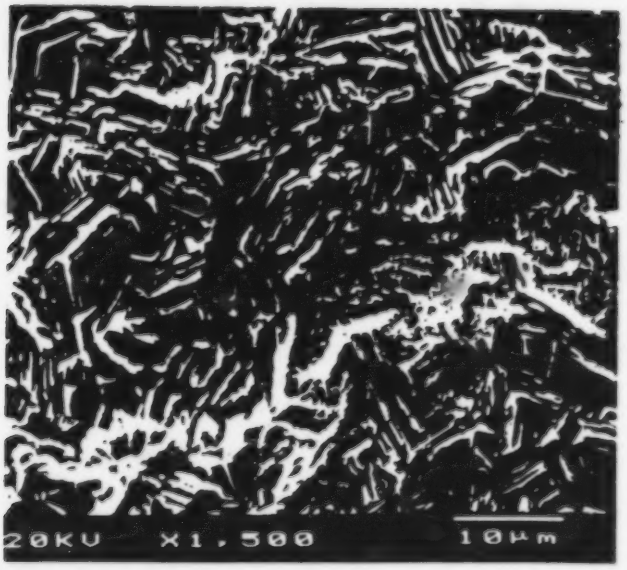

100
95
90
85
80
75
CURRENT EFFICIENCY (%)
0
0.01
0.02
0.03
0.04
ANTIMONY (mg/L)
10 mg/L Saponin
5 mg/L Saponin
3 mg/L Saponin
1 mg/L Saponin

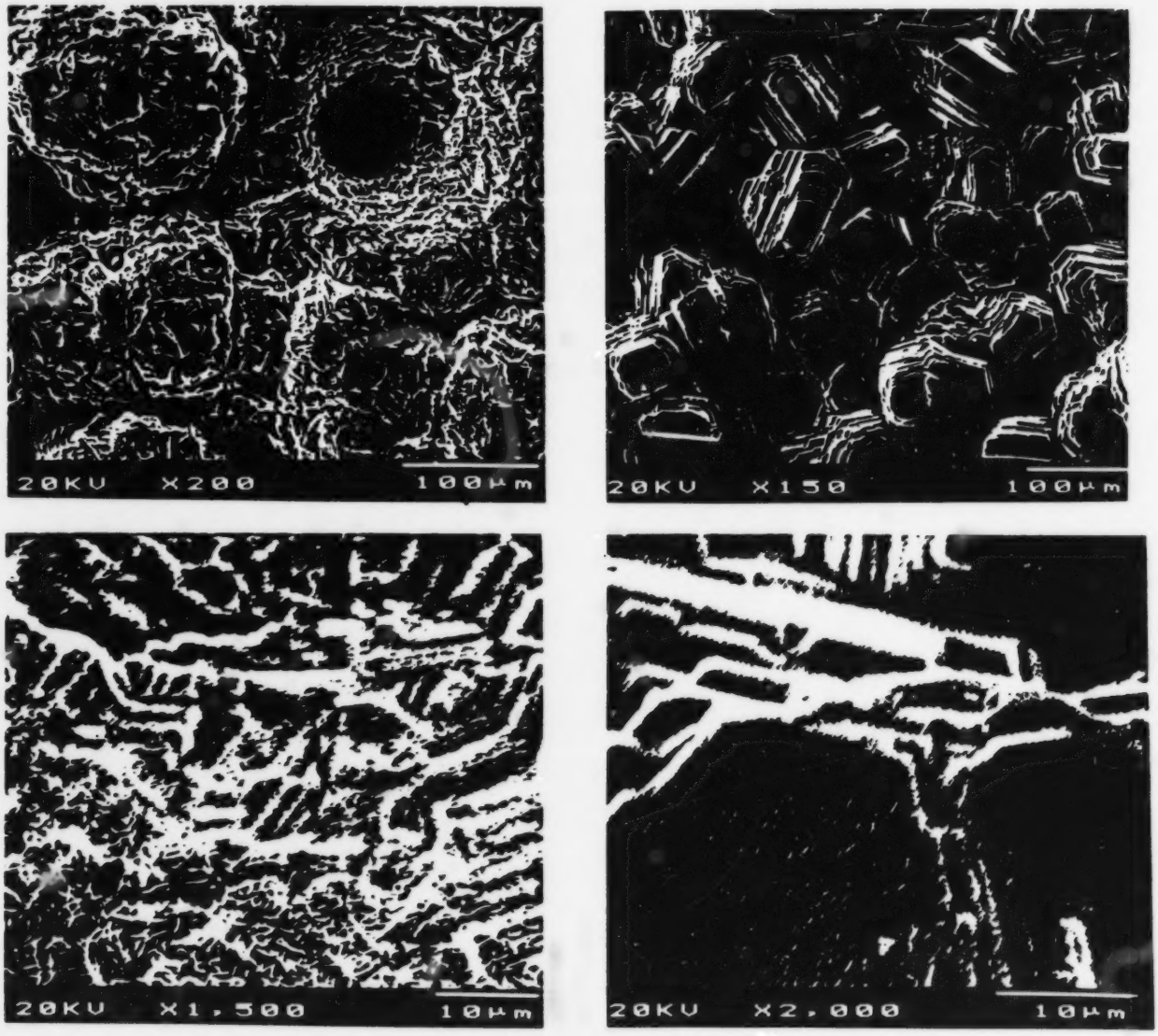
FIG. 14





10 mg/L Saponin +
0.01 mg/L Sb

Figure 15. SE micrographs showing the effect of Saponin and antimony on the morphology of a 6-h zinc deposit electrowon at 500 A/m^2 and 38°C.



a) 45 mg/L Na_2SiO_3
0.01 mg/L Sb

b) 45 mg/L Na_2SiO_3
0.04 mg/L Sb

Figure 16. SE micrographs showing the effect of sodium silicate and antimony on the morphology of 6-h zinc deposits electrowon at 500 A/m^2 and 38°C.

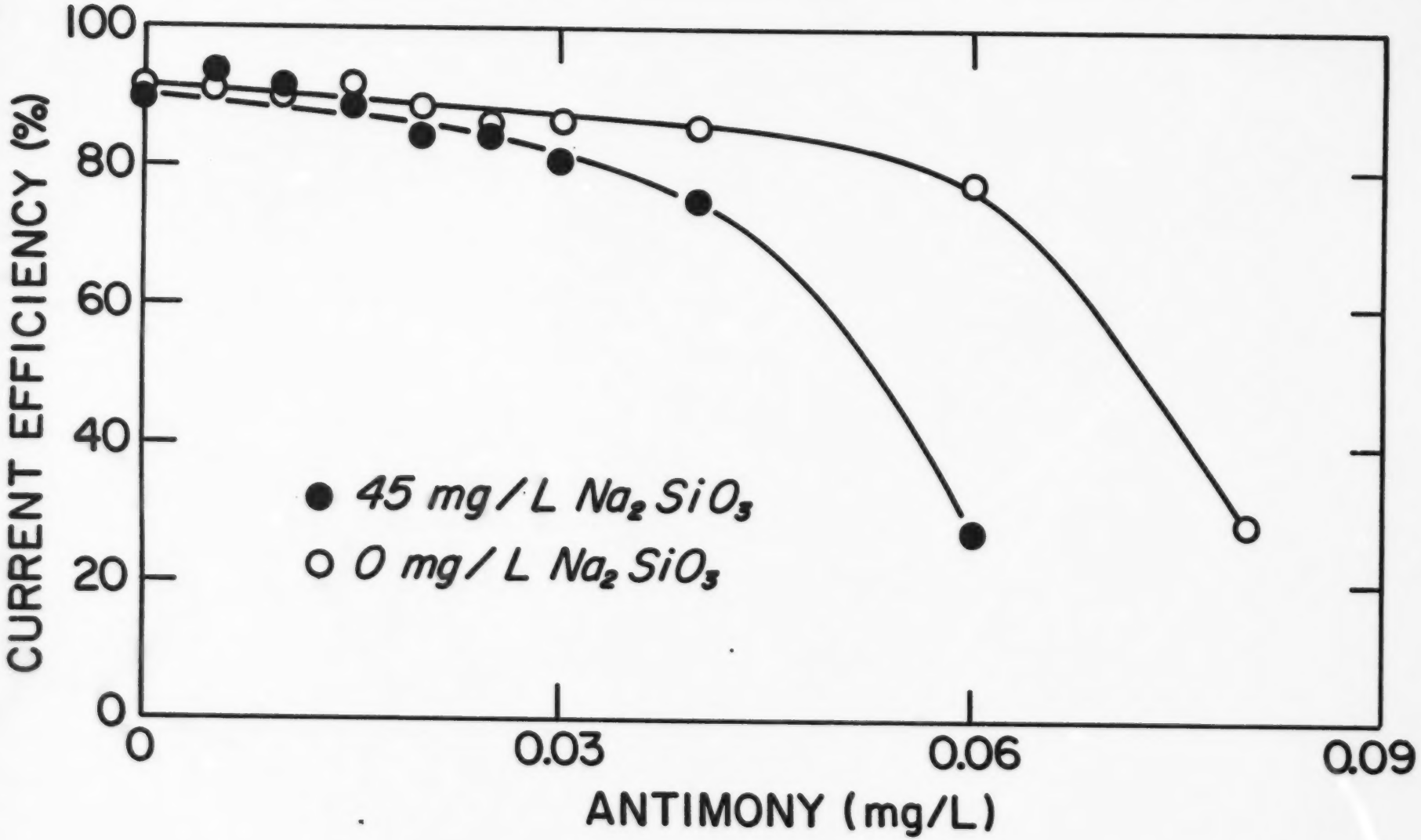
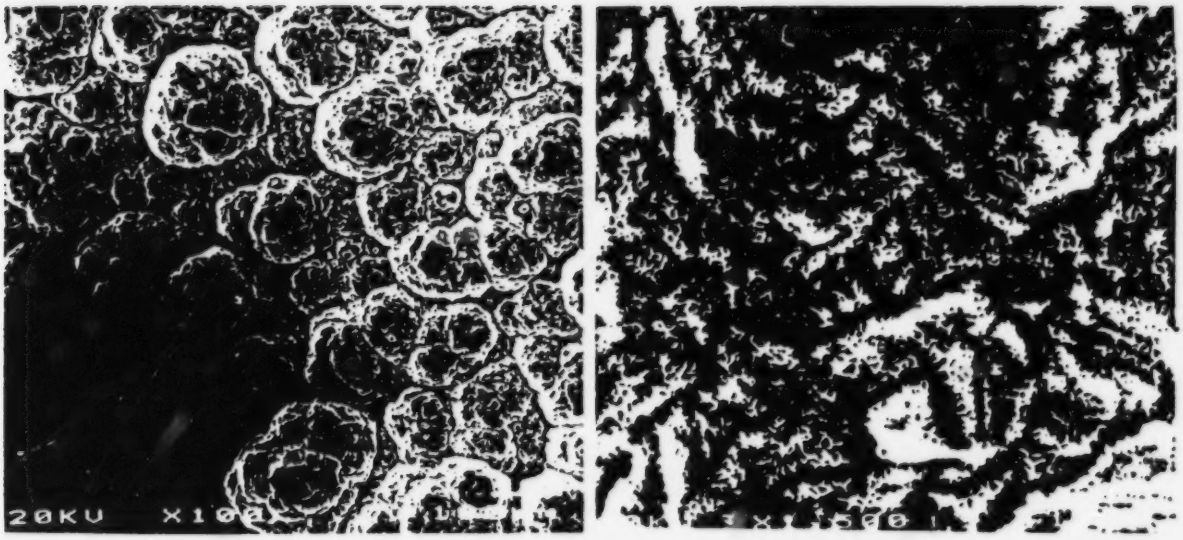
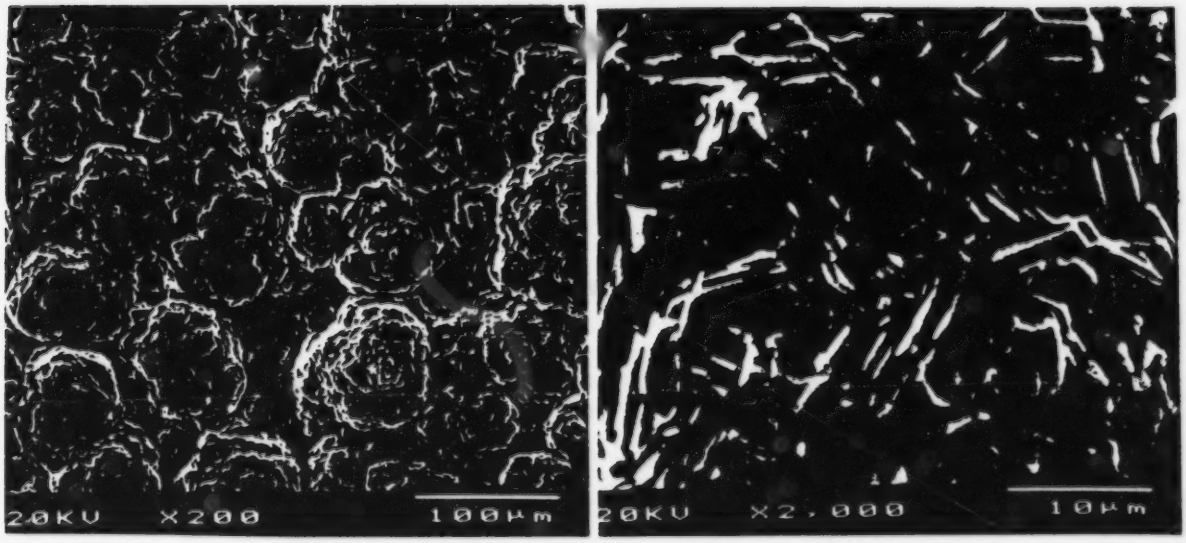

100
80
60
40
20
0
CURRENT EFFICIENCY (%)
0
0.03
0.06
0.09
ANTIMONY (mg/L)
● 45 mg/L Na_2SiO_3
○ 0 mg/L Na_2SiO_3

FIG. 17

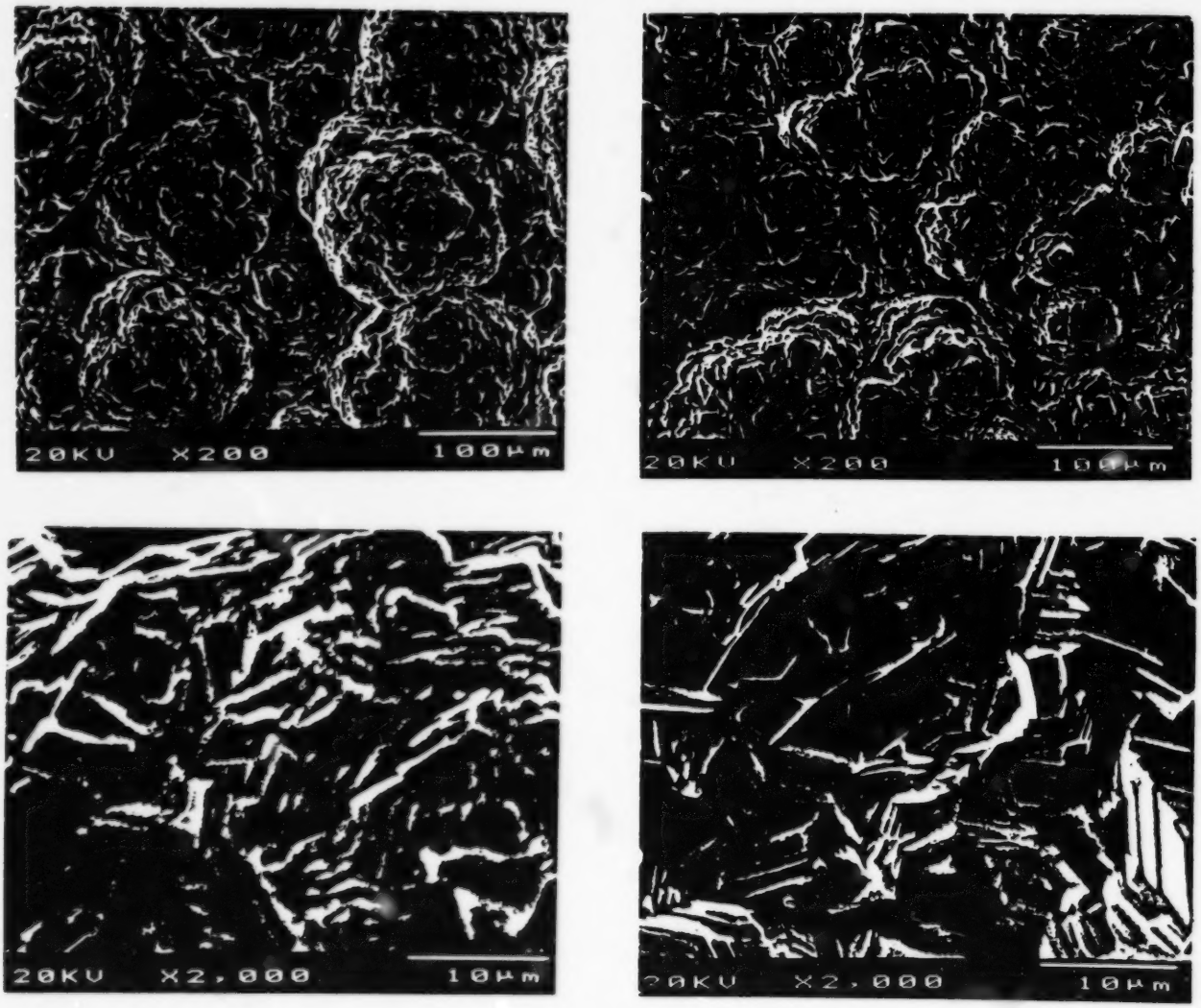


a) 3 mg/L Dowfroth + 3 mg/L Saponin + 0.005 mg/L Sb



b) 7 mg/L Dowfroth + 3 mg/L Saponin + 0.01 mg/L Sb

Figure 18. SE micrographs showing the combined effects of Dowfroth, Saponin and antimony on the morphology of 6-h zinc deposits electrowon at 500 A/m^2 and 38°C.



a) 3 mg/L Dowfroth +
1 mg/L Saponin +
0.005 mg/L Sb +
45 mg/L Na_2SiO_3

b) 7 mg/L Dowfroth +
3 mg/L Saponin +
0.01 mg/L Sb +
45 mg/L Na_2SiO_3

Figure 19. SE micrographs showing the combined effect of Dowfroth, Saponin, antimony and sodium silicate on the morphology of 6-h zinc deposits electrowon at 500 A/m^2 and 38°C.

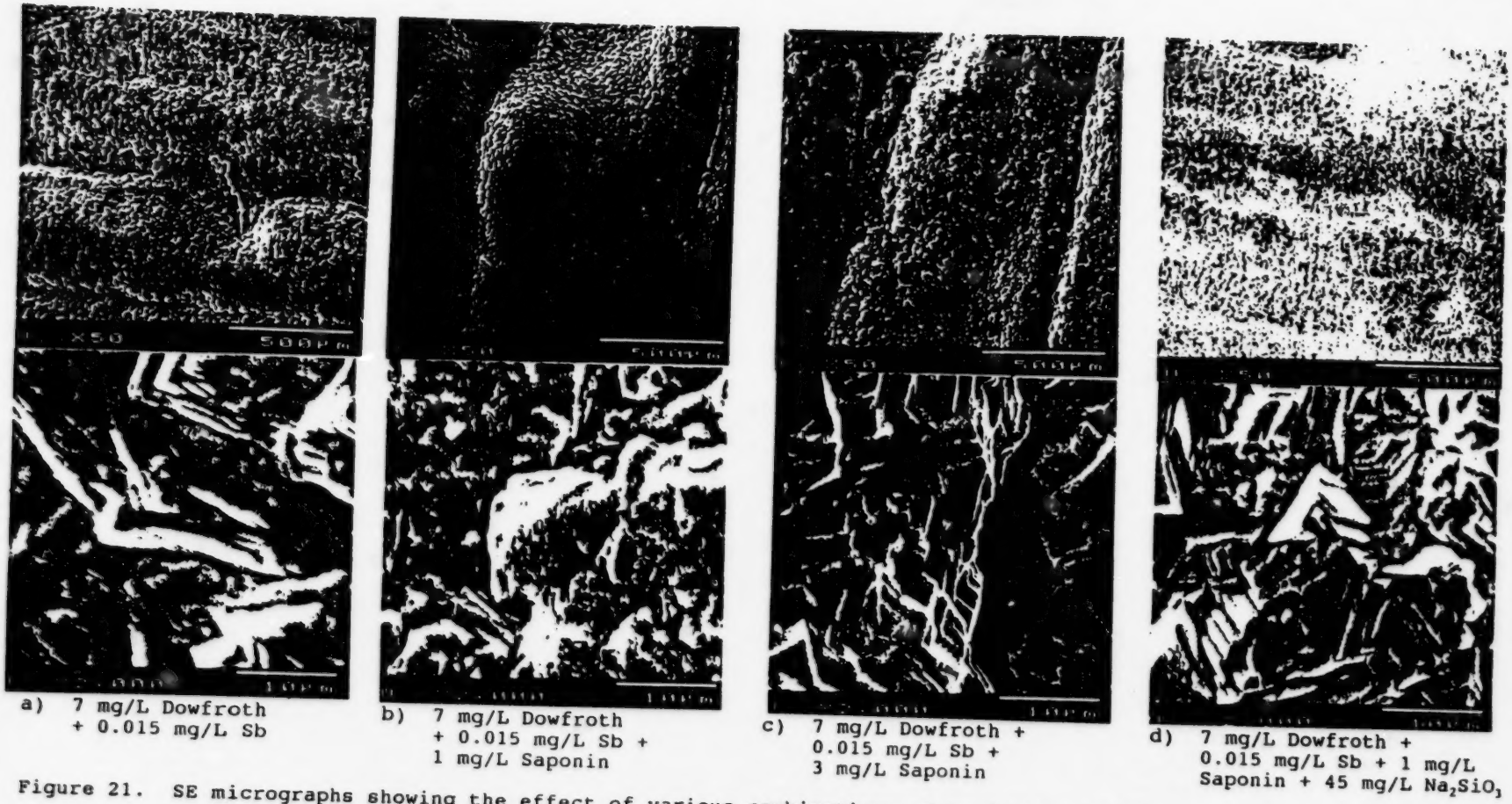
a) 3 mg/L Dowfroth + 0.01 mg/L Sb

b) 3 mg/L Dowfroth + 0.01 mg/L Sb + 1 mg/L Saponin

c) 3 mg/L Dowfroth 0.01 mg/L Sb + 3 mg/L Saponin

d) 3 mg/L Dowfroth + 0.01 mg/L Sb + 1 mg/L Saponin + 45 mg/L Na_2SiO_3

Figure 20. SE micrographs showing effect of various combinations of Dowfroth, antimony, Saponin and sodium silicate on the morphology of 24-h zinc deposits electrowon at 500 A/m^2 and 38°C.



a) 7 mg/L Dowfroth + 0.015 mg/L Sb

b) 7 mg/L Dowfroth + 0.015 mg/L Sb + 1 mg/L Saponin

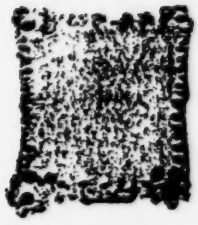
c) 7 mg/L Dowfroth + 0.015 mg/L Sb + 3 mg/L Saponin

d) 7 mg/L Dowfroth + 0.015 mg/L Sb + 1 mg/L Saponin + 45 mg/L Na_2SiO_3

Figure 21. SE micrographs showing the effect of various combinations of Dowfroth, antimony, Saponin and sodium silicate on the morphology of 24-h zinc deposits electrowon at 500 A/m^2 and 38°C.

3mg/L Dowfroth
0.01 mg/L Sb;

92.6% CE

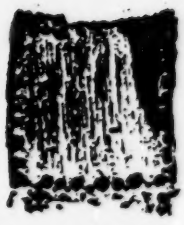


3 mg/L Dowfroth
0.01 mg/L Sb,
1 mg/L Saponin;
91.4% CE

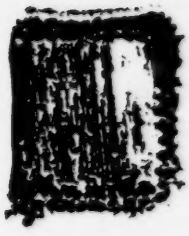
3 mg/L Dowfroth
0.01 mg/L Sb,
3 mg/L Saponin;
91.5% CE

7 mg/L Dowfroth,
0.015 mg/L Sb

90.0% CE

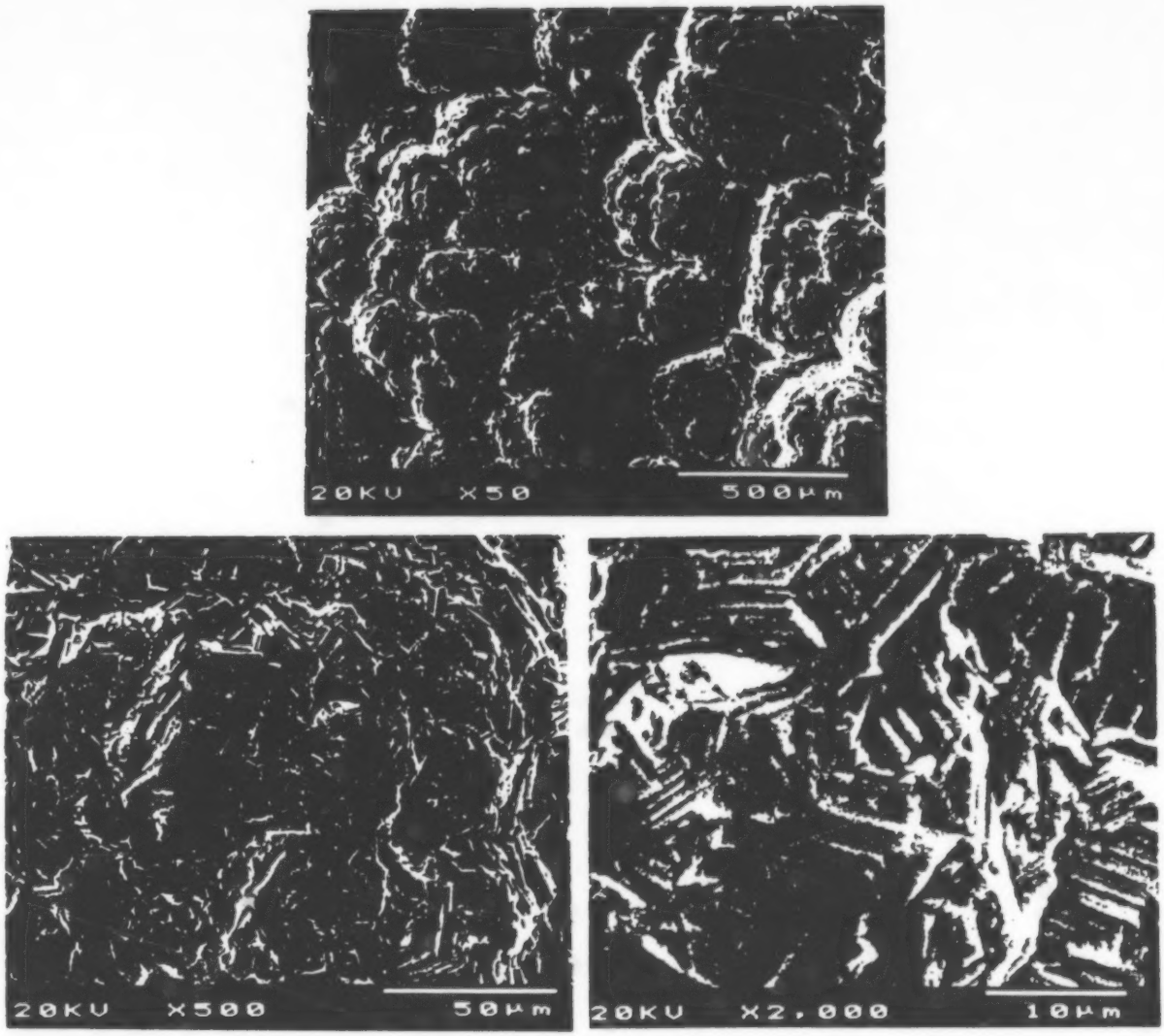


7 mg/L Dowfroth,
0.015 mg/L Sb,
1 mg/L Saponin;
89.8% CE



7 mg/L Dowfroth,
0.015 mg/L Sb,
3 mg/L Saponin;
90.4% CE

Figure 22. Photographs (1X) of various 24-h zinc deposits electrowon at 500 A/m^2 and 38°C.



5 mg/L Dowfroth + 1 mg/L Saponin + 0.015 mg/L Sb
+ 13 mg/L Na_2SiO_3 + 50-100 mg/L Sr; [101][112];
92.2% CE; 13 ppm Pb

Figure 23. SE micrographs showing the morphology of a 24-h Kidd Creek commercial zinc deposit.